# *The* TREND IN ENGINEERING

*at the University of Washington*

*In this issue:*


EXPLORER AIDS RADIO PROPAGATION RESEARCH

A KINETIC STUDY OF A SOLID-STATE REACTION

NEW TECHNIQUES IN PHOTOELASTICITY

ADSORPTION KINETICS IN THE CONVERSION OF CARBON DIOXIDE TO METHANE

ELEVENTH NORTHWEST CONFERENCE ON ROAD BUILDING



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THE ENGINEERING EXPERIMENT STATION

# ASPECTS OF MODERN ENGINEERING EDUCATION*

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DESPITE THE LONG HISTORY of engineering accomplishment behind us, it is a comparatively recent trend which renders an after-dinner speaker almost declassé unless he discusses some ramification of one of about four topics, "The Engineer Shortage," "Can We Humanize the Scientists?" "Can We Simonize the Humanist?" or "Is Sputnik Watching Us?" Why is it that technology has become a preoccupation so quickly, why as a discussion topic is Aristotle outflanked by the Atom, and Spinoza by Sputnik? The answer to this question lies not in the rate of technological progress, but in the second derivative—the acceleration of the rate of the advancement of scientific knowledge and the consequent shortening of the time beween scientific discovery and engineering design and application.

Let us imagine that our human time scale can be compressed so that one day represents 1,000 years, and thus our scientific history is written over a period of one week beginning on Sunday morning, representing 5,000 B.C. Throughout all day Sunday, Monday, and part of Tuesday no progress at all is evident. Men are living in caves; they use stone tools and muscles for power. By late Tuesday evening some stone and timber buildings are evident, and the Pyramids have been built, using human power. Bronze tools are being used on Wednesday, and oxen are pulling wheeled carts. Iron tools, hardened by tempering, are ready Thursday. Some canals and reservoirs have been constructed and by nightfall an alphabet has been invented to simplify communication. Friday morning geometry has been exploited to make accurate land surveys. The screw and pulley have been invented and the Romans are building aqueducts and highways.... On this same Friday the stone arch construction is becoming evident in large bridges, palaces and cathedrals. England's fuel wood supply has already become exhausted but the heat content of coal has been discovered to supplant it. Saturday the acceleration is apparent. Algebra and trigonometry are available as scientific tools. Magnetism has been discovered; alchemy is flourishing, cast iron is being produced in quantity; sizable boats are being built, and the invention of the magnetic compass is of great importance to their navigation. But it is only on Sunday that things really start to happen. Just before midnight Saturday, an Italian sea captain had his western trip to Asia interrupted by America, and by 3 a.m. mass migration was under way. The steam engine was invented at 7 a.m. and immediately applied to land and sea transport. The Bessemer converter announced at 9 a.m. made large quantities of steel available, followed quickly by Portland cement, rubber, and petroleum. Cheap aluminum was available by 9:30, man flew in an aeroplane before 10, Lindbergh landed in Paris at 10:25, supersonic flights were common by 11, and the first artificial satellites were in the sky before lunch.

The same morning, the nature of electricity was discovered at 6 a.m., the arc light, generator, and electric motor were in use by 9, incandescent lights by 9:30, and by 11 a.m., 100,000,000 horsepower of electricity were being used.

At 10 a.m. a physicist announced that all atoms consisted of heavy nuclei surrounded by orbital electrons. Einstein announced his theory of relativity at 10:10 and atoms were disintegrated by neutron bombardment at 10:35. At 10:53 nuclear fission was announced. I leave the extrapolation of these nearly exponential curves to your imagination.

In a similar dramatic fashion the lag between scientific discovery and engineering application has been shrinking. Hero of Alexandria in 75 B.C. demonstrated the power available in expanding steam but it was 1800 years before Newcomen invented his engine and a further 60 years before Watt added automation to make continuous attendance unnecessary. The development of electric power lagged the scientific work of Faraday and Henry by 40 years, but the invention of the wonderful transistor by Bardeen, Brattain and Shockley followed their publication on the flow of holes in semiconductors by a scant four weeks! Small wonder, then, that technology has become the focus of such close and widespread scrutiny, that engineering education is being discussed and debated so widely. and that the obvious trend in engineering curricula is to increasing emphasis on fundamental science and mathematics, on the processes of thought, rather than on learning by rote!

Against such a background it is our task to establish a modern engineering school at McMaster University. The advent of Engineering Studies is a natural development of the fine tradition of scholarship in science and mathematics which has brought distinction to McMaster for many years, and such a tradition must form the foundation of any respectable modern engineering school.

The argument for general engineering, is a persuasive one. Our fields of knowledge are merging; companies do so much on-the-job training they might prefer to employ versatile engineers who can readily be assimilated into mechanical, or electrical, or civil engineering activites. So many engineers find themselves in pursuits foreign to their field of specialization that general training might have been an advantage to them.

Despite these arguments, I disagree with general engineering on at least two counts. In the first place, a university is a community of scholars, and it must probe the depths in at least one field of endeavour. It is as necessary for the staff as for the students that work be continually directed at assailing the frontiers of knowledge, and to work at this level implies specialization.

Secondly, studies in depth cannot be postponed until entry into industry. Unless a significant fraction of new engineering techniques emanate from our colleges, those colleges certainly are failing their function. We are indeed fortunate in the enthusiastic advice and support which we receive from our many industrial colleagues and we place a very high value on it. But unqualified industrial approbation of our curriculum would be to me the surest proof that it is already outmoded and our vision limited. To provide the necessary depth in engineering studies, specialization will certainly evolve in our courses, particularly in the final year.

What will be our attitude towards humanities and social studies?

I think perhaps we engineers have been a bit too humble in accepting the onslaught of the proponents of a "liberal education"—apologists who frequently are militantly

*(Continued on page 32)*

* Excerpts from an address to the Society of Automotive Engineers, Toronto, reproduced by permission of the author.

# PROFESSIONAL ETHICS AND ENGINEERING EDUCATION

## A Rejoinder

OSCAR H. LENTZ, *Assistant Professor of Economics, Colorado School of Mines*

THE RECENT STIMULATING EDITORIAL by Mr. A. Arthur Hemenway concludes with the following statement: "Perhaps the requirement that engineering students attend a fundamental ethics course might be the best evidence that the engineering profession has a serious long-range interest in improving its ethical standards." Ordinarily, I think, one trained in philosophy would be in general agreement with Mr. Hemenway. Reflecting upon his conclusion and his thesis, however, I found myself holding to rather divergent views on the problem he discusses. If these views have any merit, I am indebted to Mr. Hemenway and his timely article for triggering their expression at this time.

Current interest in professional ethics and engineering education stems from two social pressures. The first is found within the engineering profession itself. It stems from the desires of leading engineers to achieve a more realistic alignment between the functional contributions of engineers to modern society and the degree of social and professional recognition they currently receive. The second, and more general, social pressure is external to the engineering profession. This pressure stems from the profound and rapid social changes occurring in modern society. Although analytically distinct, these social pressures are not unrelated. Mr. Hemenway has dealt with the first of these pressures. I propose to deal with the latter. In conclusion, I shall point up the normative implications of our divergent approaches to the problem of professional ethics and engineering education.

Looking down what one historian has termed "the long gun barrel of history," we cannot escape the conclusion that our age is unique in several fundamental respects. Not the least of these is the deep and pervasive social, economic, and political change occurring throughout the entire world. Some historians insist that we are living in the midst of a world revolution.

This world revolution is proceeding along two fundamental trends of sociological integration. The most apparent trend is seen in the evolutionary development of international organizations, agencies, and political institutions. For conceptual elegance, this trend may be termed "horizontal integration." The second of these trends is seen in the steady erosion of pre-industrial criteria for distinguishing social status, class, and caste. On one hand we see the rapid historical erosion of (1) monarchies, (2) aristocracies, (3) colonialism, (4) religious castes, and (5) tribal myths. On the other hand we see the rapid historical rise and steady advance of (1) organized labor, (2) minority racial groups, (3) minority religious groups, (4) democratic and quasi-democratic political parties, and (5) the disturbing successes of communist doctrines of social and economic "democracy" throughout the underdeveloped regions of the world. Such phenomena are not entirely unrelated in a broad historical perspective. One scholar has termed these phenomena "the revolt of the masses." These profound social changes point up the trend of "vertical integration" occurring in modern society.

The philosophic implication of these changes is that they reflect the emergence of new human and social values. Moreover, these new values accrue an indelibile stamp of urgency in an interdependent world community experimenting with nuclear fission and fusion and earth satellite vehicles.

The growing interdependence of modern society involves a growing web of human and social relationships. If world and local communities are healthy, these interweaving human and social relationships are conducive to new dimensions of human and social growth. The growth of interdependence also implies that this giant web of human and social relationships snarls, rots, and breaks wherever selfish or intolerant persons and groups maintain their traditional norms of behavior at the expense of the common good.

The complexities of modern living require two basic and contrary types of educational preparation. The continued development of science and technology requires increasing degrees of skill and specialized training. For many this process is long, arduous, and narrowing in its effect upon the intellect and personality. Our educational curricula have been oriented primarily to this cultural requirement. Contrary to this general requirement is the increasingly urgent requirement for technicians to maintain an over-all perspective, balance, and adaptability to human and social problems. This latter requirement involves the development of increased social awareness and sensitivity to emergent human values. Engineers are currently being forced to accept the increased social responsibilities imposed by the complexities of the modern society. Acceptance of these new social responsibilities implies that engineers are increasingly required to evaluate human and social values.

Mr. Hemenway is quite sound when he says, "A superior sense of professional ethics can come only from a superior sense of values." The point at issue concerns the most effective way to equip engineers with a superior sense of values. I cannot escape the feeling that a fundamental ethics course would be only another course in methods—with very little substance relevant to the problem.

The pedagogical issue involved can be spotlighted with reference to Mr. Hemenway's thesis concerning the relationship between ethics, values, and wisdom. "For a philosopher, the term 'ethics' implies 'values,' *and values are more a matter of wisdom than of knowledge.*" (Italics mine). This thesis strikes me as being the distillation of a distinctly pre-modern view of ethics and value theory. Contemporary value theory, like physical theory, is thoroughly contextual in character. Wisdom is born of knowledge. The knowledge that engineers need most is a knowledge of human and social values and a knowledge of how these values are changing. This knowledge can come only from the rapidly developing social sciences.

*(Continued on page 31)*

*Ed. Note: Further opinions from our readers on this almost inexhaustible subject are welcome, and will be published if space permits.*

April, 1958

# The TREND

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## *at the University of Washington*

## CONTENTS

Aspects of Modern Engineering Education
*J. W. Hodgins,* McMaster University . . . . . 1
(From an address before the S.A.E., Toronto.)

Professional Ethics and Engineering Education: A Rejoinder
*Oscar H. Lentz,* Colorado School of Mines . . . 2

"Explorer" Aids Radio Propagation Research
*H. Myron Swarm* . . . . . 5

A Kinetic Study of a Solid-State Reaction
*Earl C. Roberts* . . . . . 6

New Techniques in Photoelasticity
*Jarle Holen, E. E. Day* . . . . . 10

Adsorption Kinetics in the Conversion of Carbon Dioxide to Methane
*J. B. Romero, L. N. Johanson* . . . . . 17

Engineering Research Dividends . . . . . 25
The Snap-Action Bimetallic Thermal Disk and Its Application to Thermal Switches *E. B. Seeley*
Minor Losses in Viscous Flow *S. H. Siddiqui*
A Study of Flux Distribution and Reactivity for a Spherical Intermediate Reactor Employing an Iterative Technique for Solving the Diffusion Equations *S. Tashiro*

Road Builders Hold Eleventh Annual Meeting
*R. G. Hennes* . . . . . 27

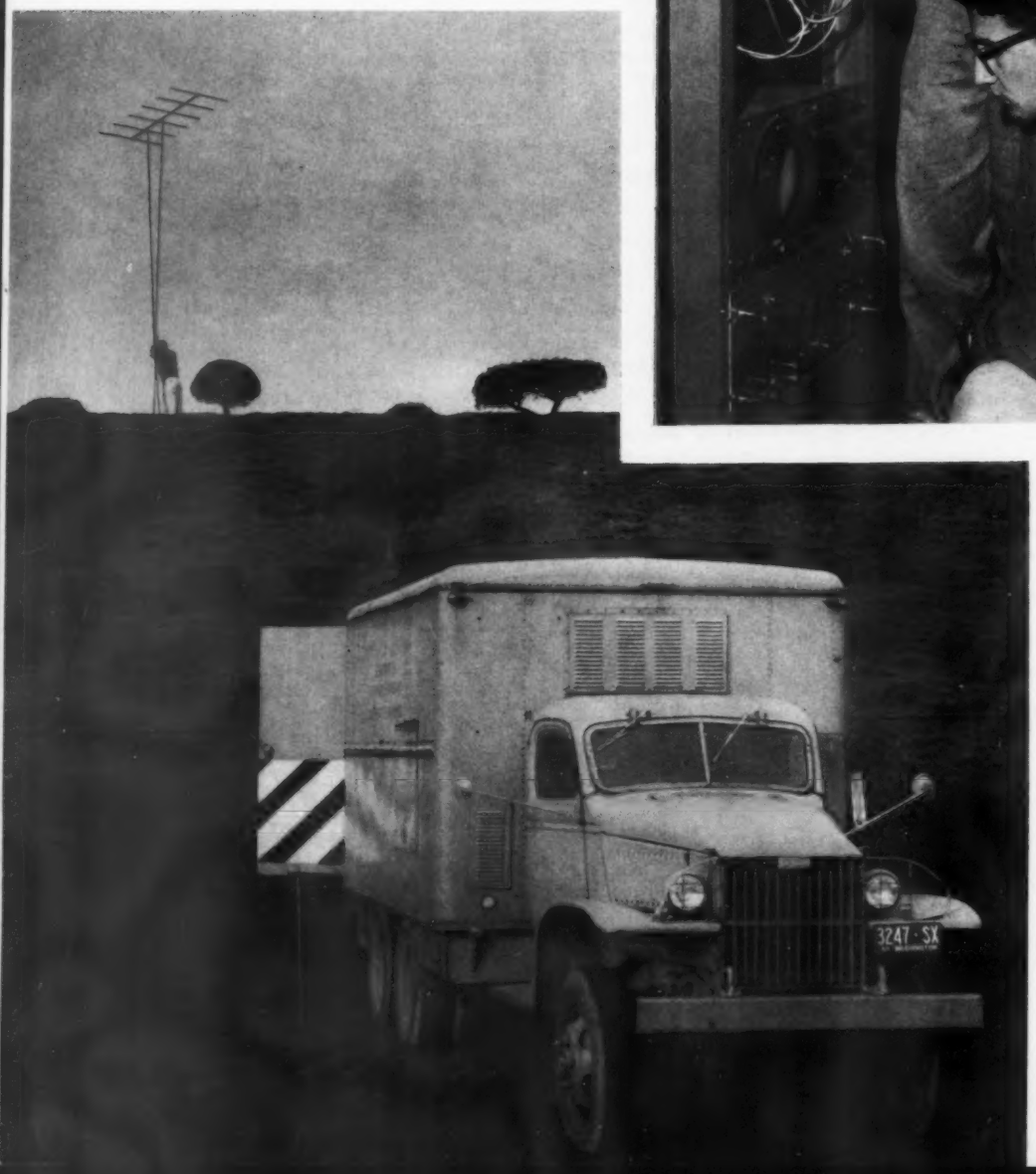
Outside U.S.A. . . . . 29
Rupture by Bending and by Shearing Stress in Reinforced Concrete Beams
Steel at High Elastic Limit in Welded Construction
Nomographic Method for Evaluating X-Ray Back-Reflection Patterns Used in the Computation of Residual Stresses in Steels
Heat Transfer During Nucleate Boiling of Liquids Under Conditions of Natural Convection
Contribution to the Study of Problems in the Utilization of Light-Weight Concretes

Notes and Comments . . . . . 30
Engineers in the News
Sewage Works School
New Chromite Extraction Process

Vehicle Maintenance and Fleet Supervisors Courses Held on Campus . . . . . 32

*RIGHT*

**Radio Propagation Research Group operating the recording equipment of the Satellite Project.** *Left to right:* **Fred Mason, electronics technician, Darrell Jackson, assistant, Dr. H. M. Swarm, supervisor.**




*LEFT*

**Field view showing truck containing Satellite monitoring equipment, and antenna mounted at top of hill.**

*Photograph courtesy Seattle Post-Intelligencer*

# "Explorer" Aids Radio Propagation Research

H. Myron Swarm

*Associate Professor of Electrical Engineering*

ON THE EVENING OF JANUARY 31, 1958, word was flashed to the American public that the U. S. Army had successfully fired a Jupiter-C rocket that put in orbit the first American satellite, the Explorer I. It was emitting radio signals at 108 and 108.03 megacycles. This was the information many research scientists throughout the world were waiting to hear. At the University of Washington the Radio Propagation Research Group of the Electrical Engineering Department immediately began final assembly of the equipment that had been procured during the previous few months. During the early fall (after the successful launching of the Russian satellites) a research project was planned to use the radio signals from both the Russian and American satellites for basic radio propagation research.

Late Friday evening and Saturday morning of February 1 testing of receiving equipment was completed. Because of the low elevation and very high noise level in the vicinity of the Electrical Engineering Building, it was necessary to move the monitoring equipment to a higher elevation and thus obtain a clear unobstructed signal path to the south. The equipment was mounted in the Electrical Engineering Department's truck and transported to the vicinity of one of the Seattle Water Department's reservoirs. Through the courtesy of Ray Heath, the Superintendent, permission was granted to park the truck at the base of the reservoir and to locate the antenna at the highest level, as may be seen in the photograph on the opposite page.

During the next week the Explorer's radio signals on 108.03 megacycles were heard each night for periods of from two to twelve minutes. The weaker signals at 108 megacycles were heard sporadically when receiving conditions allowed.

Although the path of the Explorer was such that it never came overhead in the Seattle area, the 108.03 signals were consistently heard whenever the satellite's northernmost part of the orbit passed over Arizona, California, or a few degrees west of the coast of California. Usually three successive passes of the satellite were heard. Thus the characteristic undulating high-pitched sound of the United States' first earth satellite, the Explorer I, was heard and recorded in the Seattle area.

The receiving equipment consisted of a Yagi antenna followed by a VHF converter, high-frequency receiver, and recording equipment. A six-element 108-megacycle Yagi antenna matched to a 50-ohm coaxial cable comprised the antenna system. A low-noise grounded-grid-input VHF converter translated the 108 and 108.03 signals to approximately 16 megacycles. The converted signal was then coupled to a high-frequency receiver for amplification and detection. The detected signal output was then mixed with timing signals obtained from a separate receiver tuned to WWV and recorded on a Magnecord magnetic tape recorder. The sensitivity of the system was such that a 0.12-$\mu$v signal modulated 30 per cent provided an output 6 db above the noise level.

The 108.03-megacycle signal at the input of the converter averaged approximately 0.15 $\mu$v and the maximum was approximately 0.35 $\mu$v. The 108 signal was much weaker and never exceeded 0.1 $\mu$v.

The Radio Propagation Research Group of the Electrical Engineering Department is under the writer's direction. At the present time six students are assisting in the operation and construction of equipment and the analysis of ionospheric radio propagation data. Assistants on the Satellite Project are Darrell Jackson, a sophomore in Electrical Engineering, and Fred Mason, electronics technician. This group is shown operating the equipment in the photograph opposite. Plans are now underway to expand the recording equipment and study the doppler shift, fading, and amplitude properties of the oblique incidence signals from future satellites. These data will be of inestimable value in determining information about the earth's upper atmosphere and associated radio propagation phenomena through the various ionosphere layers. This is part of the University's basic radio propagation research, and the characteristics of the satellite's radio signals will be correlated with other ionospheric data obtained from the University's vertical incidence sounding equipment and from data of other laboratories.

# A KINETIC STUDY OF A SOLID-STATE REACTION

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E. C. Roberts

## Introduction

The age-old processes of hardening and tempering steel have progressed from a stage involving considerable superstition, through an age of rather routine blacksmithing, to what has now developed into a highly scientific metallurgical study. The simple procedure of raising the temperature of a piece of steel to a high red heat and then quickly cooling to a low temperature by quenching in an appropriate medium will invariably result in a remarkable increase in hardness. However, a surprising number of factors are now recognized as being contributory in determining just what hardness is obtained. Other physical properties of the quenched piece are likewise influenced by such things as the temperature of the furnace and quenching medium, the nature of the quenching medium and, most important, the chemical composition of the steel.

The actual hardening reaction is now known to involve some important structural changes and it has been possible to recognize and analyze the crystallographic relationships between the hardened product, martensite,* and the parent, austenite,* from which it forms. Not only these relationships but the relative amounts of product formed and parent-retained in the quenched piece depend to a great extent on the composition of the steel. Thus the physical nature of quenched steel is directly related to its solid-state chemistry.

Since the tempering treatment will depend on the results obtained by quenching, the chemistry of the metal again enters the picture significantly. In this treatment we find not one but a series of overlapping reactions occurring. These are of the nucleation and growth type in which the reaction product must first form as a tiny nucleus, then develop within the surrounding matrix. Such reactions are highly diffusion-dependent, and their rates will be determined by the slowest diffusing element taking part in the reaction.

Because of the overlap encountered among the various reactions or stages of tempering, the individual stages are difficult to follow from beginning to end. However, if a diversity of experimental techniques are used to study each individual specimen, interesting correlations appear. Such experimental results, when assembled and analyzed simultaneously, have shown that in the plain carbon steels three separate and quite distinct solid-state reactions occur during tempering and, when these reactions are complete, a fully annealed equilibrium product results.

In the first stage of tempering the original martensite of a medium or high-carbon steel (0.40 to 1.4 per cent carbon—the types normally heat-treated) decomposes into a hexagonal close-packed carbide (epsilon carbide) of the approximate formula $Fe_2C$ and another martensite containing about 0.25 per cent carbon. The latter substance is a distinct product of the reaction, but it is not yet known if it develops competitively with the high-carbon martensite or merely results from its partial decomposition.

The second stage of tempering involves the decomposition of the retained austenite—generally into bainite. On the basis of recent magnetic determinations,[1] it now appears that the reaction product also initially contains some of the above-mentioned epsilon carbide. However, as in the first stage studies, the fineness of division of the reaction products makes direct diagnosis difficult even with such advanced facilities as the electron microscope.

The formation of cementite ($Fe_3C$) constitutes the third stage of tempering. Because of the relative simplicity of the products formed, this has been the stage longest known and most easily followed by a number of physical test methods. Recent electron microscope studies [2,3] also show that this is a more complex reaction than was originally assumed and that a number of substages are involved. The ultimate formation of cementite in the spheroidized condition represents the completion of the third stage in plain carbon steels.

In low-alloy steels we find that an additional reaction, or a fourth stage of tempering, must also be considered. This stage, like the third, can also be followed with relative ease because of the nature

* Martensite is a body-centered tetragonal solid solution of iron plus carbon and/or other alloying elements; austenite is a face-centered cubic solid solution of iron plus carbon and/or other alloying elements.

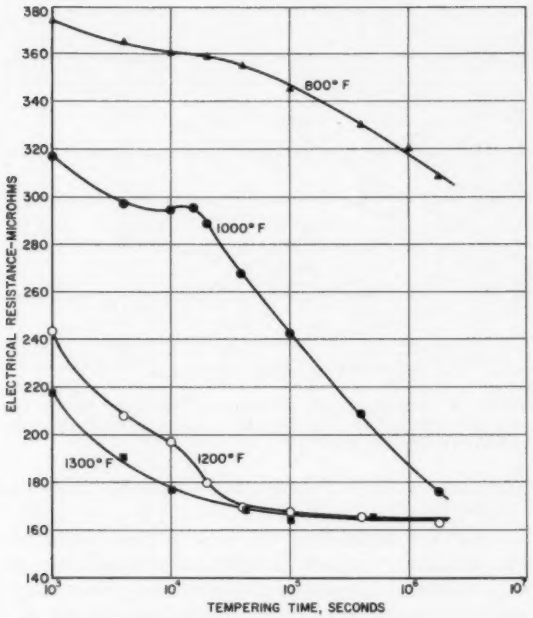


**FIG. 1. Changes in electrical resistance upon tempering at 800° F, 1000° F, 1200° F, and 1300° F.**

of the reaction products. The development of an equilibrium alloy carbide represents the reaction, and the alloy carbide forms following the initial development of cementite. The fourth stage thus interferes with the progress of the third stage and the cementite cannot spheroidize.

It is the purpose of this paper to illustrate the progress of the fourth stage reaction in a low-alloy steel. The correlation possible between the various test methods shows both the changes in physical properties and the change in the chemistry of the phases as the alloy carbide forms.

## Alloy Selection

The steel selected for these observations was a specially prepared analysis (Table I) based on previous equilibrium studies of carbide compositions in chromium steels.[4,5] This earlier work showed that, with certain chromium-to-carbon ratios in the steel, a chromium-carbide phase of the composition $(Cr,Fe)_7C_3$ would result at equilibrium. The same phase exists in certain steels in commercial production, but the special preparation eliminated the problems arising from the presence of tramp residual elements that might interfere with the reaction being analyzed.

**TABLE I**
**ANALYSIS OF STEEL USED IN EXPERIMENTAL WORK**

| C% | Cr% | Mn% | Si% |
|---|---|---|---|
| 0.68 | 4.53 | 0.31 | 0.19 |

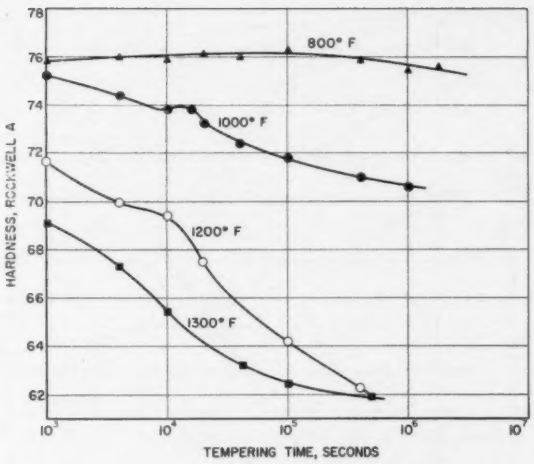


**FIG. 2. Changes in Rockwell A hardness values upon tempering at 800° F, 1000° F, 1200° F, and 1300° F.**

Preliminary experimentation with this steel involved a series of austenitizing and quenching treatments followed by metallographic studies. In summary, this initial work showed that

1) complete carbide solution in the austenite resulted following an austenitizing treatment of $2100 \pm 10°$ for thirty minutes;
2) no incipient melting occurred at the grain boundaries nor did excessive grain growth result with this treatment;
3) the specimens could be oil-quenched from the austenitizing temperature, then refrigerated in liquid nitrogen without cracking;
4) the refrigeration treatment reduced the amount of retained austenite to less than 7 volume per cent.

The importance of this last finding was that the second stage of tempering was virtually eliminated and the reaction results to be studied would involve only those arising from the third and fourth stages. Previous work on a steel of closely similar composition had delineated the temperature range in which the fourth stage reaction occurred.[6] Consequently, a recheck and confirmation of the temperature range determined was all that was required for the particular composition chosen in this investigation.

## Experimental Work

The tempering treatments were carried out in molten alloy or salt baths controlled to $\pm 5°$ F. Bare specimens were used for the shorter tempering times while specimens sealed in evacuated pyrex tubes were used for the longer runs. Following completion of the heat treatment, the individual specimens, which were three inches long, were carefully polished on a high-speed lathe from their initial

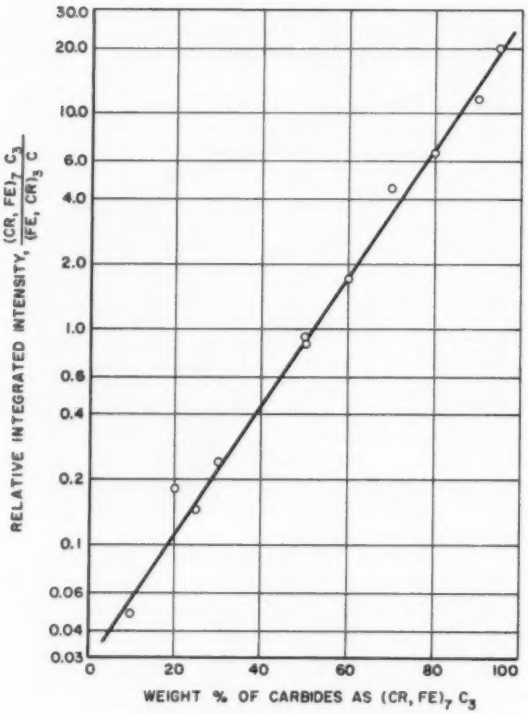


**FIG 3. Calibration curve for determining the relation between the relative integrated intensity ratio of chromium carbide to cementite and the weight per cent of carbides as $(Cr, Fe)_7C_3$.**

diameter of 0.260 down to approximately 0.250 in. Electrical resistance measurements were then made on the specimens, using a device which involved heavy copper current contacts at the extreme ends of the specimens and a pair of parallel fixed knife edges 1½ in. apart. A current of approximately 50 amp was momentarily supplied by an automobile battery, and the potential drop between the knife-edge contact points against which the specimen was held by a clamping device, was determined by means of a Kelvin Double Bridge.

In order to minimize the thermal component of resistance and thus accentuate the changes due to structural transformations, measurements were made in a liquid nitrogen (–196° C). Following the completion and rechecking of the resistance measurements, a series of accurate diameter determinations were made by the use of a vernier micrometer and a set of measuring wires allowing an accuracy of ±0.0001 in. At least seven diameter measurements were made along the 1½-in. section of the specimen used for electrical resistance measurements. The electrical resistance measurements were then corrected to a standard cross section of 0.2500 in.

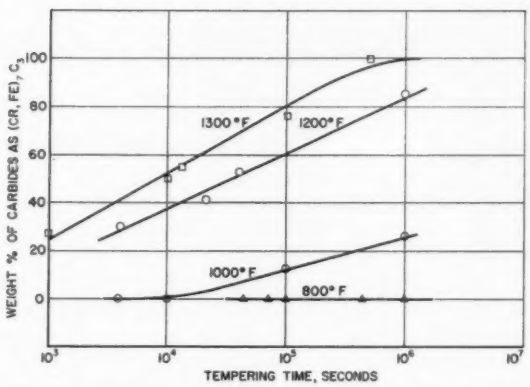


**FIG. 4. Experimental relationship between weight per cent of carbides as $(Cr, Fe)_7 C_3$ and tempering time for various temperatures.**

diameter and are accurate to within ±1 microhm (Fig. 1).

After the completion of the electrical resistance measurements, a determination of the hardness of each individual specimen was made. The Rockwell A scale (Brale indentor with 60-kg load) was adopted because of the wide range of hardness values encountered. At least five hardness values on each individual specimen were determined and an average was taken.

In order to be reassured that the hardness and electrical resistance deviations from a smooth curve were not due to experimental error, a series of specimens were tempered to the temperature and time range where the deviations were found. Confirming evidence that a very real change was occurring was indicated by the results obtained (Fig. 2).

Upon completion of the hardness measurements, the individual specimens were made the anodes in a complex electrolytic cell in which separate chambers for the anolyte and catholyte solutions were joined by a fritted glass membrane. The use of this complex cell was justified by the fact that the anolyte was a neutral solution (pH=7) and the neutrality remained constant during the electrolysis. In this cell the carbides could be separated conveniently from the surrounding metal matrix because of the preferential dissolution of the latter during electrolysis. Upon complete decomposition of the steel specimen, the extracted carbides were removed from the anolyte chamber, carefully washed successively with hot water, alcohol, and ether, and dried in a vacuum oven at approximately 170° C. The dried carbides were then made into appropriate samples for an X-ray diffraction analysis.

The X-ray diffraction analysis was carried out by choosing a characteristic line for each carbide from the diffractometer pattern of pure cementite

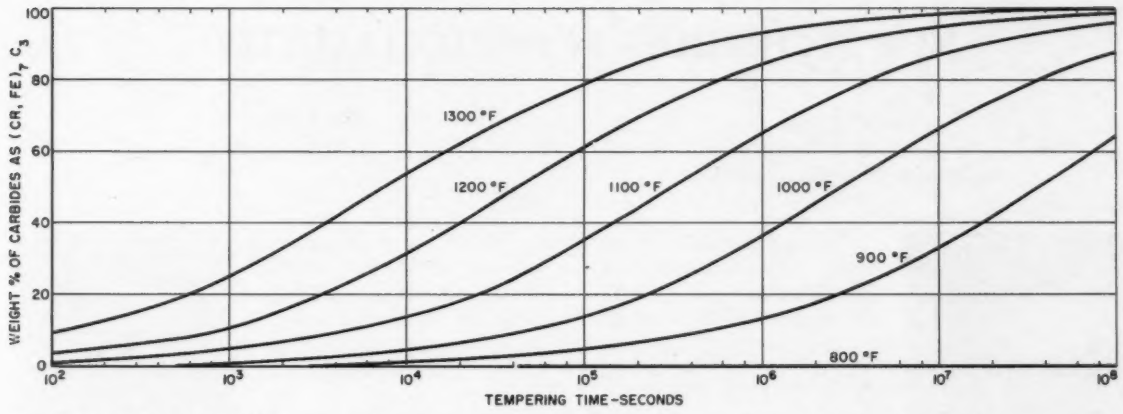


**FIG. 5.Calculated relationship between weight per cent of carbides as $(Cr, Fe)_7 C_3$ and tempering time for various temperatures.**

and pure chromium carbide. These lines were relatively close together in their $2\theta$ values, and yet did not overlap in the diffraction pattern obtained from the carbide mixtures. By using a series of weighted mixtures of pure cementite and pure chromium carbide and measuring the areas enclosed by the diffraction peaks of the lines selected, it was possible to plot a reference curve which provided the basis for the analysis of the relative amounts of cementite and chromium carbide in the carbides extracted from individual steel samples (Fig. 3).

The relative integrated intensities of the chosen lines for each extracted residue were then used in conjunction with the calibration curve in order to determine the chromium carbide-to-cementite ratio in the individual steel samples. A review of the plots of the electrical resistance and hardness diagrams shown in Figs. 1 and 2 indicates that a marked increase in resistance and an accompanying hardness change occur at the same point that chromium carbide is found to appear in the X-ray diffraction analysis, i.e., at about $10^4$ seconds at 1000° F (Fig. 4).

The fact that an electrical resistance increase and a change in hardness result from the initial precipitation from the chromium carbide, tells us that some coherency must exist between the initial chromium carbide and the matrix. However, the rapid decrease in hardness and electrical resistance which follows in a short time interval shows that this coherency is very short-lived.

A second change in hardness and electrical resistance also was found to occur at about $10^4$ seconds at 1200° F. This change was not indicated in the X-ray diffraction results of the carbides and hence is probably due to a structural change in the matrix.

Calculations based on the X-ray diffraction results for a specific amount of chromium carbide formation, e.g., when $(Cr, Fe)_7C_3$ represented 30 weight per cent of the carbides present, at the various temperatures used, showed that the activation energy for the fourth stage carbide development was of the order of 58,000 cal/mol. This compares very favorably with the most recent determinations for the activation energy for diffusion of chromium in alpha iron. Thus the kinetics of formation of $(Cr, Fe)_7C_3$ apparently are controlled by the rate of chromium diffusion in the solid solution.

Utilizing this information and the experimental points from the highest tempering temperatures (the most dependable data), idealized curves can be calculated for the rate of formation of $(Cr, Fe)_7C_3$ in this steel at a series of temperatures. The reaction kinetics seem to follow those given by the expression:[7]

$$\frac{df}{dt} = \frac{k\,(1-f)\,f}{t}$$

in which $t$ = time in seconds
$k$ = reaction constant
$f$ = fraction of $(Cr, Fe)_7 C_3$ formed in time, $t$.

The resulting curves are shown in Fig. 5. By this mathematical analysis it is possible not only to extend the time range of the determinations but to calculate the results that should be obtained at other temperatures within the tempering range.


## SUMMARY

Primarily by the use of X-ray diffraction analysis of extracted carbide residues from a steel tempered in the range of the fourth stage of tempering, it is possible to determine the rate of formation of $(Cr,Fe)_7C_3$ in a chromium steel. The results show that the kinetics of formation follow a specific type


*(Continued on page 31)*

# NEW TECHNIQUES IN PHOTOELASTICITY*

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During the last few years many new techniques in photoelasticity have been developed which have greatly increased the usefulness of photoelasticity, and have helped it to become one of the standard methods of experimental stress analysis. Fringe sharpening and fringe multiplication are two new techniques which have been described in a paper by Daniel Post, a photoelastician at the Naval Research Laboratories in Washington, D.C. From his paper it appears that fringe sharpening in many instances could considerably increase the accuracy of the photoelastic method, and that fringe multiplication has the advantage that only small loads need be applied to the model. The purpose of this study was to build the necessary equipment and to investigate the possibilities of these two techniques.

## Equipment

The conventional photoelastic polariscope has to be modified slightly to make it suitable for fringe sharpening and fringe multiplication. The polariscope must be such that a nearly collimated beam of monochromatic light traverses the model. Two partially reflective mirrors are also required, with one mirror mounted on each side of the model and parallel to it. The mounting of the mirrors must permit one of them to be rotated a few degrees about any axis in its own plane, and also both of them as a unit to be rotated in a similar manner. The mounting should further be designed so that the distance between the mirrors can be varied, since it is important to have the mirrors as close to the model as possible. Several pairs of mirrors with different reflective properties should be available, because the optimum reflectivity depends upon the particular investigation. Three pairs of mirrors were used in these experiments. Their characteristics at a wavelength of 5461 Å are listed in Table I.

E. E. Day

One of the problems associated with fringe sharpening and fringe multiplication is the low intensity of illumination of the final image. The intensity of the brightest points in this image can be less than 1 per cent of the intensity of the original light beam. For the equipment used in this work, which had a 100-w A-H4 mercury vapor lamp as light source and an incident light beam 2½ in. in diameter, it was found that the final image could be made only 1 in. in diameter for it to be reasonably bright. To reduce the light losses, the frosted glass in the observation screen was replaced with a clear glass, and the image was viewed with a special eyepiece. By using this method the image in most instances could easily be focused, observed, and photographed. The film used, Super Ortho Press, is extra sensitive to green light, and the exposure time was therefore usually less than 30 sec.

TABLE I
MIRROR CHARACTERISTICS

| Mirror Pair No. | Reflectivity (%) | Transmittivity (%) | Absorptivity (%) |
|---|---|---|---|
| 1 | 71.5 | 28 | 0.5 |
| 2 | 85 | 13 | 2 |
| 3 | 93 | 5 | 2 |

## Fringe Sharpening

In photoelasticity it is necessary to find the fringe order locations in the model before the stress distribution can be determined. When the fringe order at a specific point has been found, the difference of the principal stresses at this point is determined from Eq. 1,

$$\sigma_1 - \sigma_2 = \frac{F \cdot C}{d}, \qquad (1)$$

where $\sigma_1, \sigma_2$ = the principal stresses,
$d$ = model thickness,
$C$ = photoelastic constant of the material,
$F$ = fringe order at point in question.

The accuracy of the method is therefore partly dependent upon how well the fringe order distribution

* Condensed and arranged by the authors from Mr. Holen's thesis submitted for the degree of M.S. in Mechanical Engineering, 1957.

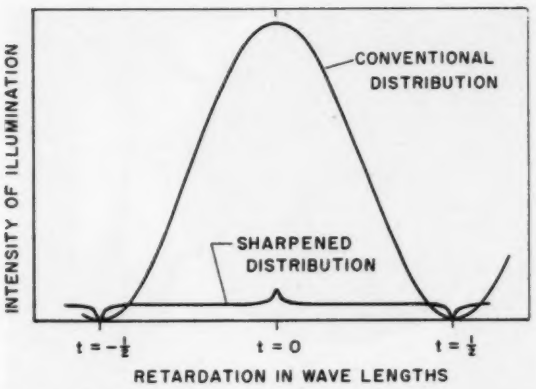


**FIG. 1. Variation of intensity of illumination across any conventional fringe compared with intensity distribution across a sharpened fringe.**

in the model can be determined. This distribution is found from the isochromatic fringe pattern of the model. The location of a particular fringe order is only a line, but the fringe from which this location is to be determined may be quite wide. The fringe pattern is due to the interference caused by the birefringent model. Across any fringe, the distribution of the intensity of illumination follows Eq. 2,

$$I = I_0 \cos^2 \pi t \,, \qquad (2)$$

where $I$ = intensity of illumination,
$I_0$ = maximum value of intensity of illumination,
$t$ = relative retardation in wavelengths of the two light vectors emerging from the model.

If a light field polariscope is used, the full fringe orders will be located at the points where $\cos^2 \pi t = 1$, and the half orders where $\cos^2 \pi t = 0$; in other words at the brightest and the darkest points. For a dark field polariscope, the opposite holds true. The variation of $t$ with distance $s$ across a fringe may be quite complex, and the distribution of the intensity is usually skewed. If the fringe at the same time is wide, it may be difficult to locate the fringe order accurately.

Fringe sharpening changes the intensity distribution across the fringe. Figure 1 shows the conventional distribution and a sharpened distribution. On a black and white photograph the sharpened fringes will appear as relatively sharp lines, while the intermediate areas appear gray. A comparison of the two distributions shows that the fringe orders can be located more accurately with the sharpened fringes.

Figure 2 shows the model, the mirrors, and an incident light ray. For the sake of demonstration,

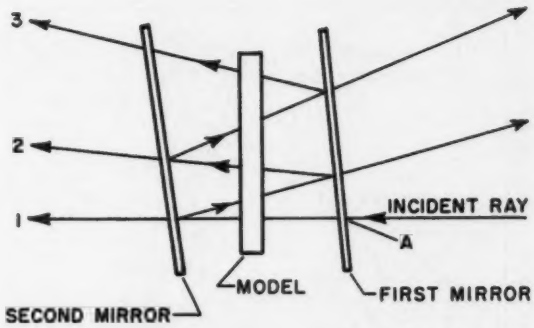


**FIG. 2. Sketch showing how an incident light ray is reflected and transmitted by two partially reflective mirrors.**

the mirrors are shown not quite parallel with the model, but at a slight angle with it. The incident ray strikes the first mirror at A; here part of it is reflected and part of it passes through the mirror and strikes the model. As the ray passes through the model it is split into two mutually perpendicular vectors, and a relative retardation, $t$, will take place between them. Upon emerging from the model the two vectors interfere and form a new ray with an intensity different from that of the one that entered. As this ray strikes the second mirror part of it is reflected and part of it passes through and will eventually reach the observation screen. The reflected part will again pass through the model and after a second reflection part of it, in turn, will eventually reach the screen. When the mirrors are parallel with each other and perpendicular to the incident ray, Rays 1, 2, 3, ... on Fig. 2 will all emerge from the same point and strike the observation screen at the same point. But, whereas Ray 1 has traversed the model only once, Ray 2 has traversed it three times, Ray 3 five times, and so on. The intensity that these rays produce on the screen will be the combined effect of all of them. If the light in the incident ray has most of its light within a bandwidth of 25 Å or more, into which most so-called monochromatic light sources fall, it can be shown that the combined intensity of all the rays equals the arithmetic sum of the individual intensities. If the incident ray in Fig. 2 is replaced by a collimated beam of monochromatic light, this beam will behave in a manner similar to that of the incident ray. When the mirrors are parallel with each other and perpendicular to the incident light beam, the result will be a series of light beams superimposed on each other at the observation screen. Let

$R$ = reflectivity of each mirror,
$T$ = transmittivity of each mirror,
$I_0$ = intensity of incident light beam.

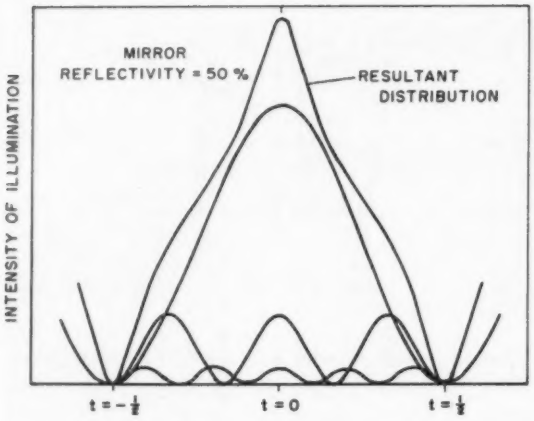


**FIG. 3. Graphical summation of the three first terms of the series that occur in fringe sharpening.**

Assuming the magnification and the transmittivity of all optical components except the mirrors as unity, the beam that corresponds to Ray 1, Fig. 2, will have an intensity distribution across a particular fringe that follows the equation,

$$I_1 = I_0\, T^2 \cos^2 \pi t.$$

This is the same distribution as that in Eq. 2 except that the intensity is reduced by the factor $T^2$ because of the mirrors. The beam that corresponds to Ray 2 will traverse the model three times. From Eq. 1 it can be seen that this beam will have three fringes for every fringe the first beam displays. The intensity of this beam is further reduced because of the two reflections it experiences. The intensity distribution for this beam becomes

$$I_2 = I_0 T^2 R^2 \cos^2 3\pi t.$$

The equation for the third beam similarly becomes

$$I_3 = I_0 T^2 R^4 \cos^2 5\pi t.$$

The resultant intensity distribution becomes the arithmetic sum of an infinite number of such beams, and it has been shown analytically that the sum of the series is

$$I = \frac{I_0 T^2}{2}\left[\frac{1}{1-R^2} + \frac{(1-R^2)\cos 2\pi t}{1+R^4-2R^2\cos 4\pi t}\right]. \qquad (3)$$

Figure 3 shows the first three terms of the series added graphically. The resultant distribution shows only a small amount of sharpening, because the mirror reflectivity is only 50 per cent. The sharpened distribution shown in Fig. 1 corresponds to a reflectivity of about 90 per cent.

The maximum intensity of illumination, or the peak intensity, in Eq. 3 occurs where $t$ equals an integer. The peak intensity of the fringe pattern determines the brightness of the pattern or the ease with which it may be observed or photographed. The peak intensity becomes

$$I_p = I_0 \frac{T^2}{1-R^2}.$$

With the approximation $T=1-R$ (Table I), the expression reduces to

$$I_p = I_0 \frac{1-R}{1+R}. \qquad (4)$$

**FIG. 4. Conventional fringe pattern of portion of a plate with a central circular hole, subjected to axial tension.**

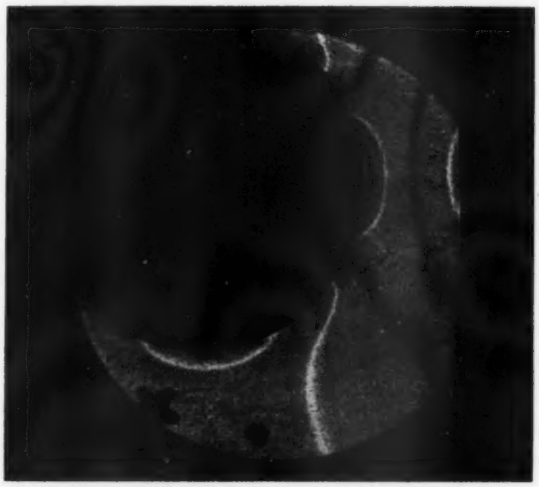

**FIG. 5. Sharpened fringes of model used in Fig. 4 subjected to the same load.**

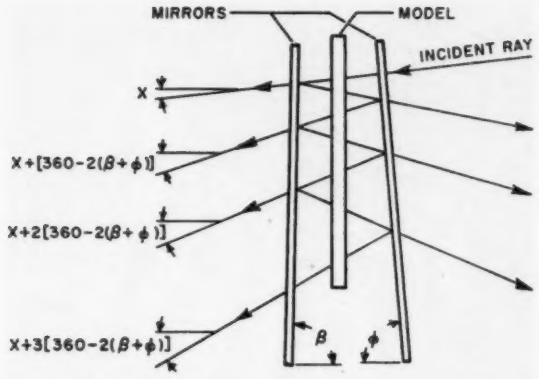


FIG. 6. Sketch showing the different directions taken by light rays emerging from the second mirror.

A study of Eq. 3 reveals that the sharpening increases with the mirror reflectivity. From Eq. 4 it is also seen that the peak intensity decreases with increasing mirror reflectivities, and approaches zero asymptotically. It was found, however, that the reflectivity should be at least 80 per cent in order to get a reasonable amount of sharpening. At reflectivities above 90 per cent the pattern becomes very sensitive to transverse variations in stress and transverse deflections in the model. In such cases the different intensity distributions that are added become distorted, and the peak of the final distribution is easily wiped out, leaving the area a uniform gray.

Experimentally, very few difficulties are involved in rotating the mirrors so that they are perpendicular to the incident light beam and parallel with each other and the model. This is accomplished by watching certain images and reflections as the mirrors are rotated. Figure 4 shows the conventional fringe pattern of a portion of a plate, with a central circular hole, subjected to axial tension. The plate was 3¼ in. wide and ⅛ in. thick, and the hole was 2 in. in diameter. Figure 5 shows the same model subjected to the same load, but with the fringes sharpened. The mirror reflectivity is 93 per cent. These two patterns clearly illustrate the advantage of fringe sharpening; the fringes are considerably sharpened, especially those representing half orders. It is interesting to note that the zero order, which is represented by a small black dot near the edge of the hole in Fig. 4, disappears in Fig. 5. This is because the zero order is actually located at the very edge of the hole. The conventional fringes in Fig. 4 could have been made narrower and more plentiful by increasing the load. But in many instances an increase in load is not possible because the model will fracture or become overstressed.

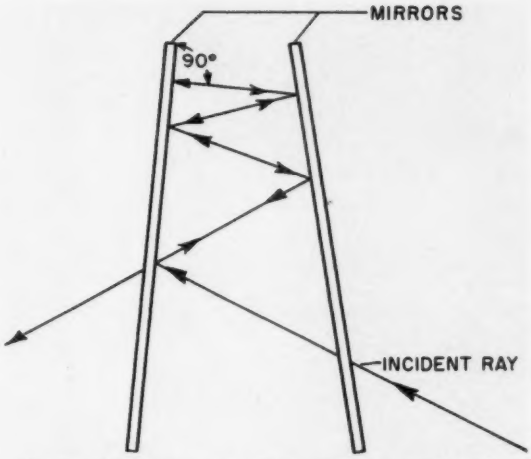


FIG. 7. Mirror arrangement for fringe multiplication to improve accuracy of the method.

## Fringe Multiplication

The primary source of information in photoelastic work is the isochromatic fringe pattern of the model. In some instances, however, large areas of the model, or even all of it, may not display any fringes. From Eq. 1 it is apparent that such a condition will exist if the model thickness or the applied load is small. Slices from a three-dimensional frozen model, for instance, may have to be cut very thin, and the load applied to a model with a notch in it must be kept low in order to prevent fracture. In such cases one ordinarily has to employ instruments like a babinet compensator to find the locations of fractional fringe orders, and this is usually a tedious process. The method of fringe multiplication increases the number of fringes so that even fractional fringe orders can be determined from the fringe pattern.

Fringe multiplication is directly related to fringe sharpening. The instruments employed are identical, but the mirrors instead of being parallel are at a slight angle with each other. From Fig. 6, which shows an incident ray, the model, and the two mirrors, it is seen that the direction of the rays emerging from the second mirror is a function of the number of times the ray has traversed the model. If a beam of collimated monochromatic light is substituted for the incident ray, the beam will behave in a similar manner. If a lens is placed behind the second mirror, this lens will collect each of the collimated light beams that emerge from the mirror in a separate point. By placing the eye or the camera lens behind any of these points, the model can be observed in light that has traversed it a certain number of times. From Eq. 1 it is evident that when the model is observed in light that has

FIG. 8. Conventional fringe pattern of portion of plate with central hole, subjected to a very small load.

FIG. 9. Fringe pattern of Fig. 8 multiplied 7 times, with the same load.

traversed it, for example, five times, the pattern will exhibit five times as many fringes as it would without the mirrors. The appearance of the individual fringes will be the same as that in conventional photoelastic patterns, but most of the fringes will represent fractional fringe orders. The effect on the fringe pattern is actually the same as that of a decrease in the photoelastic constant of the material.

Figure 6 shows that only a small fraction of the incident light will eventually reach the observation screen, and also that the peak intensity in the fringe pattern decreases with the number of fringe multiplications. The peak intensity of the light beams that emerge from the second mirror can be represented by the following series,

$$I_1 = I_0 T^2;\ I_3 = I_0 T^2 R^2 \ldots\ldots I_N = I_0 T^2 R^{N-1},$$

where $N$=multiplication factor, or the number of times of times that the beam has traversed the model. With the approximation $T=1-R$, the general term of the series becomes

$$I_N = I_0 (1-R)^2 R^{N-1}. \qquad (5)$$

Equation 5 shows that there is an optimum value of the reflectivity for any particular value of the multiplication factor. By differentiating the equation, this optimum value is found as

$$R_{\text{OPT.}} = \frac{N-1}{N+1}. \qquad (6)$$

An important observation can be made from Fig. 6. It is clear that a particular ray does not traverse the model at a unique point as it ideally should, but rather at a number of different points. The accuracy of the method is therefore largely dependent upon how small the distance along the model can be kept from where the ray enters to where it eventually leaves. It is further seen that this distance increases

1) as the sum $(\beta+\phi)$ is decreased,
2) with the mirror separation,
3) at an increasing rate with the number of multiplications.

The maximum practical value of the sum $(\beta+\phi)$ is mainly dependent upon the quality of the optical components in the polariscope. (The absolute maximum of this sum is considered to be 180°, i.e., when the mirrors are parallel.) Because of imperfections in the lenses and lack of collimation in the incident light beam, the different beams that emerge from the second mirror will not be collected in points, as previously stated, but rather in spots of finite areas. The inclination of the mirrors must be large enough to completely separate these spots, so that the camera lens can take in light from only one particular beam. The finer the optical components are, the smaller will these spots be, and the less mirror inclination will be needed to separate them. The mirror separation is usually limited by the model thickness. The reflective sides of the mirrors should be facing each other, and the mirrors brought as close to the model as possible. When the mirror arrangement of Fig. 7 (slightly different from that of Fig. 6) is used in fringe multiplication, the incident light beam is reflected back and forth till it strikes the second mirror perpendicularly and from there follows its own path back. The beginning of the zigzag path is thus utilized twice, improving the accuracy considerably, especially for larger multiplication factors. The accuracy of the method can be further

improved by investigating one region of the model at a time. The mirrors can then be inclined in such planes that the zigzag path of the light rays advances in the general direction of the fringes in that particular region. From the foregoing discussion it is clear that certain inaccuracies are introduced when fringe multiplication is used. These inaccuracies occur as a displacement of the fringes from their true positions and also as a change in the distribution of light across the fringes. Experimentally it was found that this displacement approximately doubles for every increase of 2 in the multiplication factor. This means that, once the inaccuracies become appreciable, any further increase in the multiplication factor will result in an almost useless fringe pattern. The usefulness of fringe multiplication is therefore largely dependent upon the maximum number of multiplications that can be made with only a reasonable sacrifice in accuracy. For a given model thickness, this number is mainly a function of the quality of the lenses used. With the polariscope used for these experiments, a model thickness of $\frac{1}{8}$ in., and 11 multiplications, the displacement of some of the fringes was as much as $\frac{1}{8}$ in. It is believed, however, that with a better lens system this number of multiplications can be doubled with the same accuracy. Other factors that can limit the maximum number of multiplications are the brightness of the pattern and transverse model deformations. From Eq. 6 it is seen that for 9 multiplications the optimum mirror reflectivity is 80 per cent. Using this value in Eq. 5 reveals that the peak intensity in the light beam emerging from the second mirror is only 0.7 per cent of the incident intensity. Lack of brightness in the final image can usually be corrected, however, by making the image smaller or by using a stronger light source. Transverse deformations cause the light rays to be refracted every time they pass through the model. If the deformations are large, the refracted rays can be thrown out of the field of the camera lens and thus cause the particular area to appear dark on the fringe pattern.

Figure 8 shows a conventional fringe pattern; the model is the same as that used in Figs. 4 and 5 but the applied load is much smaller. Because of the small load, the fringes are wide and scarce. Figure 9 shows the same model subjected to the same load but with the fringes multiplied 7 times. The mirror reflectivity is 71.5 per cent.

**The Isochromatic Fringe Pattern Near a Crack**

The fringe pattern in the vicinity of a crack in a plate is difficult to obtain with conventional photoelastic methods because the high concentration of stress at the root of the crack causes the model to fracture before a useful fringe pattern is developed.

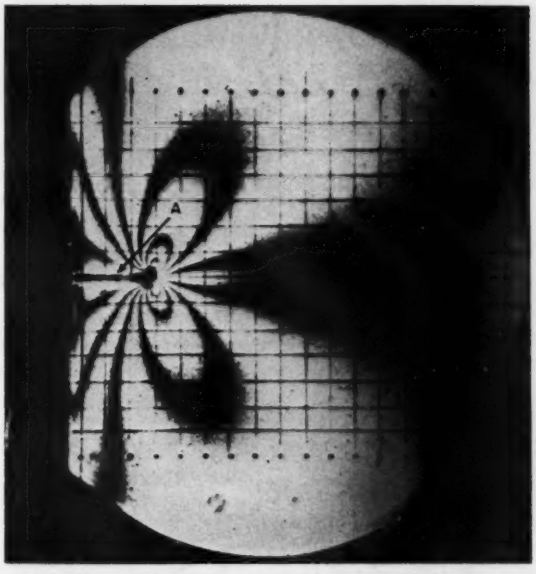


**FIG. 10. Fringe pattern of plate with edge crack subjected to tension. Note dark area at root of the crack, due to large lateral deformation.**

The use of fringe multiplication, however, will produce an almost complete fringe pattern because the applied loads are relatively small.

The model used in this experiment was of rectangular shape, 14 in. long, $2\frac{7}{16}$ in. wide, and $\frac{1}{8}$ in. thick. The crack was cut at the middle of, and perpendicularly to, one of the long sides of the model. The crack was $\frac{3}{8}$ in. deep and 0.01 in. wide. A tensional load was applied along the longitudinal centerline.

In the first part of the test the applied load was increased gradually until the model fractured, so that the maximum load that the model could be subjected to in subsequent load applications could be determined approximately. The maximum safe load arrived at was 100 lb. Figure 10 shows the fringe pattern of a portion of the model. The applied load is 87 lb and the multiplication factor, 5. The darkness of the area immediately surrounding the root of the crack (A) is due to the transverse deformation in this region. The fringe orders here could therefore not be determined. This meant that the boundary stresses could not be determined and that such methods as the membrane analogy or the electrical analogy could not be used to separate the individual stresses inside the model. However, it was of interest to plot the fringe order distribution inside the model. A matrix of shallow lines was inscribed on the surface of the model, and the fringe order at every intersection was determined. The fringe orders were then corrected with Hook's Law

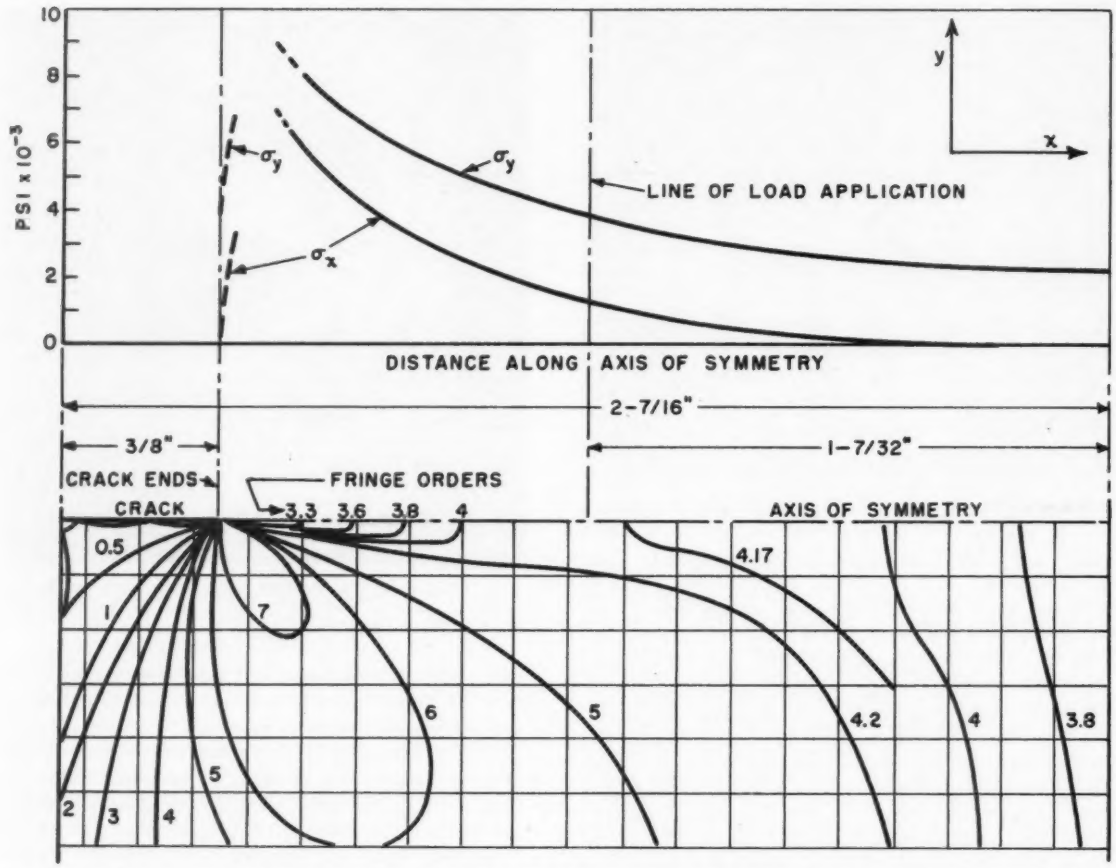


FIG. 11. *(Above)*: **Plot of principal stresses along the axis of symmetry in the vicinity of a crack. Broken lines indicate probable values.** *(Below)*: **Fringe pattern of part of the same model.**

to an equivalent applied load of 1000 lb and the results were plotted as shown in Fig. 11.

An attempt was made to find the individual stresses along the axis of symmetry. The fringe orders along this axis were found up to about $\frac{3}{16}$ in. from the root of the crack. The difference of the principal stresses could then be found from Eq. 1 and the known fringe orders. To find the sum of the principal stresses the shear difference method was used, using the isoclinic fringe pattern. A plot of the individual stresses as far as they could be determined is also shown in Fig. 11.

An interesting observation can be made from the fringe pattern in Fig. 11, where the fringe order values along the axis of symmetry decrease as the root of the crack is approached. If this trend continues to the root of the crack, it means that the highest stresses are not at the surface of the crack, but a short distance inside the model. The broken lines in Fig. 11 indicate such a stress distribution.

## CONCLUSIONS

Fringe sharpening and fringe multiplication are easily produced, once the necessary equipment is available. The equipment is of simple construction and can be attached or removed from most photoelastic polariscopes without difficulty.

Fringe sharpening improves the accuracy of the photoelastic method. However, since the accuracy in conventional photoelastic work is usually quite good, its frequent use may not be warranted.

With fringe multiplication, fractional fringe orders can be obtained directly from the fringe pattern, which is often an advantage. Some difficulties associated with this technique, such as sensitivity to transverse deformations and inaccuracies at high multiplication factors, somewhat limit its usefulness.

Finally, it should be pointed out that an instrument such as the babinet compensator can, after a very tedious point-by-point investigation, accomplish

*(Continued on page 31)*

# ADSORPTION KINETICS IN THE CONVERSION OF CARBON DIOXIDE TO METHANE*

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J. B. Romero

The design of a reactor for a catalyzed gaseous reaction usually involves the interpretation and utilization of the results of laboratory kinetic studies. Quite frequently the interpretation is based upon the Langmuir form of adsorption isotherm. Normally, the "adsorption" equilibrium and rate constants which appear in such an equation are evaluated by fitting the results of reaction rate experiments to the equation. Few attempts have been made to compare the magnitude of such constants, or indeed the form of the equation itself, with the results obtained from adsorption measurements for the same system. Agreement of adsorption and reaction kinetic results would strengthen the theoretical foundation and simplify the study of applied kinetics. Marked disagreement would suggest the need of a basic model other than the Langmuir isotherm.

This work comprised one of a series of attempts to make such a comparison. The reaction between methane and carbon dioxide was selected for the study as representative of the reaction of simple gaseous molecules on a metal-base catalyst. Also, the kinetics of this system have been studied extensively.[1]

This work was undertaken with five objectives in mind: (1) to investigate the value of a flow system as a technique for adsorption rate studies, (2) to study the rates of chemisorption for the reaction $CO_2+H_2=CH_4+H_2O$, (3) to determine chemisorption rate and equilibrium constants for the individual reactants and compare them with those available from reaction studies, (4) to determine what effect, if any, one component (or components) has on the chemisorption rate of another, and (5) to attempt to elucidate the reaction mechanism.

Binder and White[1] studied the kinetics of the conversion of carbon dioxide to methane,

$$CO_2+4H_2\rightarrow CH_4+2H_2O\,,$$

in a flow system. They were able to correlate their data by two mechanisms. One involves the reaction of at least two dissociated hydrogen molecules with an adsorbed carbon dioxide molecule; the other involves the reaction of a carbon dioxide molecule with at least four dissociated hydrogen molecules. These mechanisms are designated as method "A" and "B," respectively, by these authors. One possible use of these data is to shed light upon which mechanism is the more probable one.

L. N. Johanson

In this work, adsorption rates were studied at temperatures close to 500, 600, 700, and 750° F, and pressure close to one atmosphere on ⅛-in. supported nickel catalyst pellets. The following six systems were studied: $N_2$-$H_2$; $N_2$-$CO_2$; $N_2$-$H_2O$; $N_2$-$CH_4$; $N_2$-$CO_2$-$CH_4$-$H_2O$; and $H_2$-$CH_4$-$H_2O$. In all calculations it was assumed that only one component was chemisorbed, and that all others acted as inerts. The calculated results are, therefore, valid only if this is definitely shown to be so.

The rates were studied in a flow system similar to that used by Binder and White.[1] Analysis was done continuously, where possible, by infrared analysis; otherwise, individual samples were collected and analyzed. The catalyst, temperature range, and pressure were chosen to correspond closely to those used by Binder and White so that a comparison of the two methods could be made more easily.

## THEORY

### Chemisorption on a Single Site

Equations governing activated adsorption on a single site can be obtained by a method similar to that presented by Hougen and Watson.[2] In this theory it is assumed that all active centers have the same activity and undergo the same reaction and that enthalpy and entropy of adsorption are constant with amount adsorbed. These assumptions are the same as those made by Langmuir in his derivation of his adsorption equations. If, for activities

* Condensed and arranged by the authors from Mr. Romero's M.S. thesis, 1957.

pressures are substituted, the common Langmuir adsorption equations result.

The reaction may be assumed to proceed as follows.

$$A+l=A\cdot l,$$

where $A$ is the reacting gas molecule, $l$ is the solid surface site, and $A\cdot l$ is the complex formed.

The net rate is given by,

$$r=k_A a_{Ai} C_l - k'_A C_A . \tag{1}$$

At equilibrium, $r$ equals zero and the equation becomes

$$K=\frac{k_A}{k'_A}=\frac{C^*_A}{a^*_{Ai}\,C^*_l} . \tag{2}$$

If $L$ is the number of molal active centers, then,

$$C_l=L-C_A \tag{3}$$

and

$$C^*_l=L-C^*_A \tag{4}$$

Substituting for $k'_A$ from Eq. 2 and $C_l$ from Eq. 3 in Eq. 1 and rearranging, the following form can be obtained:

$$\frac{r}{a_{Ai}}=k_A L-C_A k_A-\frac{C_A k_A}{a_{Ai} K} .$$

As shown, this equation cannot be plotted linearly. However, it is of the least squares type and if data are available for $r$, $a_{Ai}$, and $C_A$, the constants can be evaluated.

**Dissociation on a Dual Site**

The theory for chemisorption with dissociation is also presented in the literature.[2] For the case where the molecule first adsorbs on a dual site and then dissociates, with the adsorption reaction controlling the rate, the expression giving the rate is

$$r=\frac{s}{2L}\left(k_{A_2} a_{A_{2i}} C^2_l - k'_{A_2}\frac{C^2_{Al}}{K'_A}\right). \tag{5}$$

Similar treatment of this equation yields the following result:

$$\frac{r}{C^2_{A_2}}=\frac{s k_{A_2} C^2_l}{2L}\cdot\frac{a_{A_{2i}}}{C^2_{A2}}-\frac{2s k_{A_2}}{L K_{A_2}} . \tag{6}$$

This equation cannot be plotted linearly unless $C_l$ is known. This term can be written in terms of $C_{A_2}$ as $L-2C_{A_2}$, but since in Eq. 6 it is squared, a very cumbersome form of the equation results. It is much better to regard $C_l$ as constant. This quantity will be essentially constant under two conditions: (1) if $L$ is much larger than $C_{Al}$, and (2) if $C_{Al}$ does not vary appreciably.

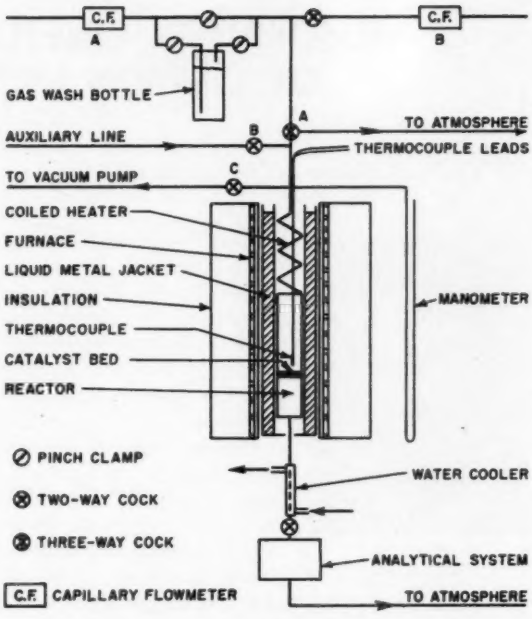


FIG. 1. FLOWSHEET OF ADSORPTION RATE APPARATUS

Making the assumption of constancy of $C^2_l$ and setting this quantity equal to its equilibrium value, $C^{*2}_l$, a plot of $\frac{r}{C^2_{A_2}}$ versus $\frac{a_{A_{2i}}}{C^2_{A_2}}$ should result in a straight line of slope, $\frac{s k_{A_2} C^{*2}_l}{2L}$, and negative intercept, $\frac{2s k_{A_2}}{L K_{A_2}}$.

Dividing the slope by the intercept, one obtains a constant in terms of $K_{A_2}$, or $K_{A_2} C^{*2}_l = \frac{\text{(4) (Slope)}}{\text{(Intercept)}}$.

## EXPERIMENTAL

**Equipment and Materials**

The reaction and analytical system was designed to yield data for the calculation of instantaneous values of $r$, $a_A$, and $C_A$. One of the major problems was the minimizing of time lag between reactor and gas-analysis equipment. This problem exists chiefly because of the speed of the reaction, equilibrium being approached in about one minute.

Figure 1 schematically illustrates the flow-metering unit, the reactor and its furnace, and the analytical unit. Gas flowmeters were coiled capillary tubing with mercury manometers. Calibration indicated a linear relationship between volumetric flow rate and pressure differential, as was expected.[3] These

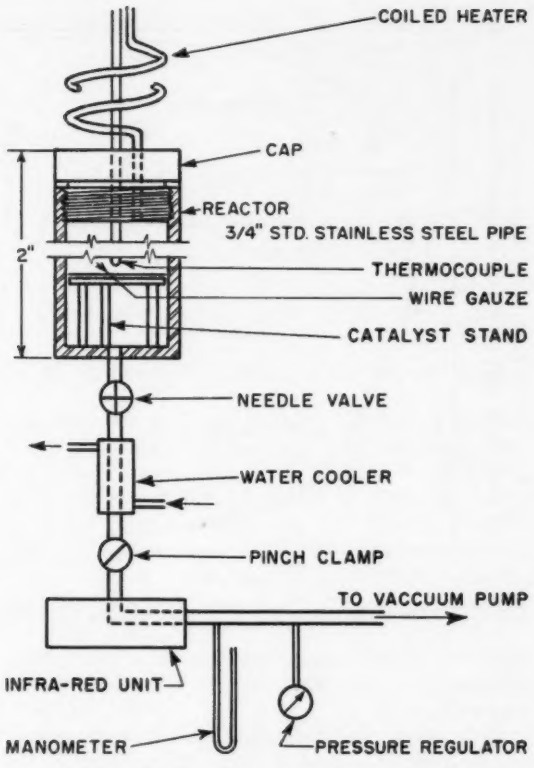


FIG. 2. REACTOR AND ANALYTICAL SYSTEM

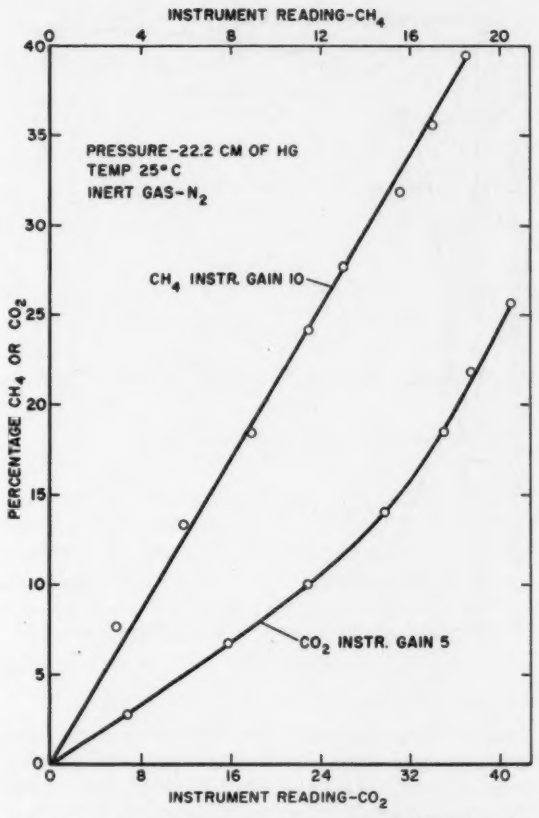


FIG. 3. INFRARED CALIBRATION CURVES FOR $CH_4$ AND $CO_2$

calibration curves and similar details may be found elsewhere.[4]

The smaller of two reactors, holding approximately three grams of catalyst, was used for all but the $N_2$-$H_2$ system of gases. Infrared gas analysis was used in situ with this reactor. Analysis of the $N_2$-$H_2$ system was by microcombustion, and the larger reactor, holding approximately 20 grams of catalyst, was used for this system, with intermittent sampling. With either reactor, heating was done electrically with a 21-amp nichrome wound furnace surrounding a liquid lead bath. The reactor was placed within the two-inch copper tube serving as the inside wall of the lead bath. Temperature control was obtained with a Wheelco Model 2627 current controller on the furnace. This system maintained constant reactor temperature conditions to $\pm 2°$ F during the course of a run (three minutes maximum).

The catalyst was obtained from the Harshaw Chemical Company, Cleveland, in the form of ⅛-in. by ⅛-in. cylindrical pellets, designated as M O.104T ⅛. This was the same type of catalyst, though not the same lot, as that used by Binder and White in their kinetic studies. Manufacturer's analysis indicated 60 per cent total nickel, 0.15 per cent $SO_4$. Carbon dioxide, nitrogen, and hydrogen used were obtained from Western Oxygen, Inc., Seattle. These gases were of research grade of guaranteed purity 99.5 per cent. Methane, obtained from the Matheson Company, Inc., East Rutherford, New Jersey, was of C.P. research grade, with a guaranteed purity of 99 per cent.

Details of the smaller reactor unit, consisting of a coiled heater, the main body, and the analytical system, are shown in Fig. 2.

The preheater consisted of 40 inches of coiled ⅛-in. stainless steel tubing of wall thickness 0.026-in., and was silver soldered to the cap of the reactor. The cap was screwed to the reactor and the connection was made vacuum tight by a copper gasket.

The analytical system consisted of the infrared analyzer, the manometer, and the pressure regulator. The analyzer is a research type, Model 15, nondispersive Infra-Red Analyzer, purchased from Liston-Becker, Stamford, Connecticut (now Scientific Instruments Division, Beckman Instruments, Inc.). Complete instrument details and instructions for operation can be obtained from the manufacturer.

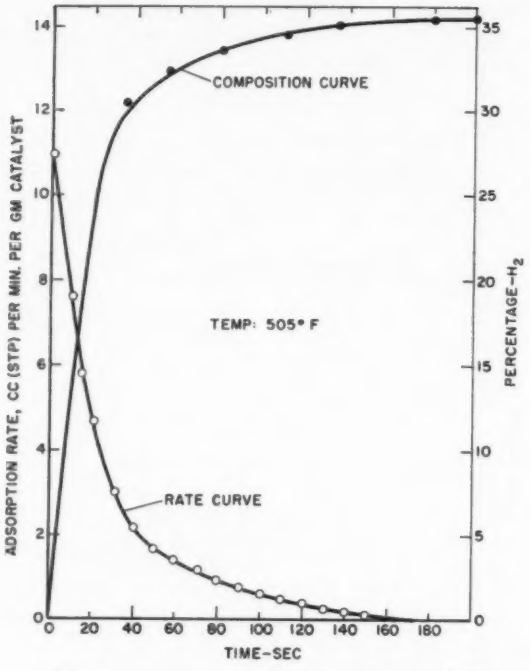


FIG 4. COMPOSITION AND RATE CURVES FOR $N_2$–$H_2$

Analysis depends upon the difference in the rate of adsorption of infrared rays by two detector cells separated by a gold foil diaphragm. The gas sample to be analyzed is passed through a cell in the path of one of the detector cells. This absorbs infrared radiation in a selective manner characteristic of the particular gas, and the same gas in the detector cell thus receives less radiation. The differential pressure, due to unequal heating, causes the gold foil to deflect, changing the capacitance of an electrical detecting circuit. The length of the sample cells, the window material used, and the pressure, depend upon the infrared spectrum of each gas. Thus, quartz windows, 22.2-cm Hg pressure and a ⅝-in. cell length were used for $CO_2$ analysis. For $H_2O$ analysis, $CaF_2$ windows, 1-atm pressure, and a 2-in. cell length were used. Calibration curves obtained were as shown in Fig. 3. If gases having infrared absorption bands overlapping those of the gas to be analyzed were present, they were "blanked out" by means of a filter cell containing the gas.

**Procedure**

Gases were premixed, with nitrogen used as an inert carrier. Water vapor and/or methane was also added to some samples of $N_2$-$H_2$ and $N_2$-$CO_2$ to study the influence of these product gases upon the adsorption of the reactant gases. Adsorption of $H_2$ and $CO_2$ in the presence of each other was not attempted since both are adsorbed and their reaction was to be avoided.

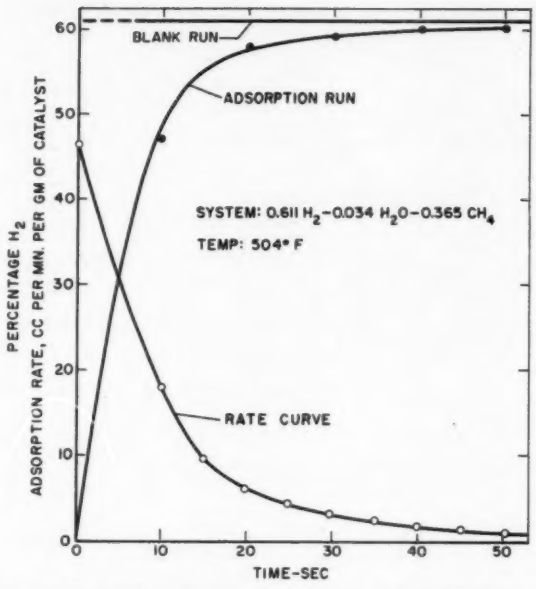


FIG. 5. COMPOSITION AND RATE CURVES FOR $H_2$–$CH_4$–$H_2O$

With catalyst and reactor in place at the desired temperature, the catalyst was reduced with hydrogen for about one hour, and the reactor and analyzing system flushed with nitrogen. After the reactor and analytical system were evacuated, feed gases were admitted and instrument readings obtained versus time.

Somewhat modified procedures were used for the $H_2$-$CH_4$-$H_2O$ system and the $N_2$-$H_2$ system. The former system was analyzed by zeroing the infrared analyzer for the premixed gas composition and flushing the instrument with methane just prior to the run. Decreasing readings with time were thus obtained. Hydrogen was then obtained by difference, since it was the only gas adsorbed. In the $N_2$-$H_2$ system, because of the larger reactor volume, it was necessary to prefill the evacuated reactor from an auxiliary tank prior to introducing feed, in order to avoid upset of the flow manometers. Sampling was done intermittently for this system, and individual samples were analyzed later by the Blacet, McDonald, Leighton microgas analyzer.[5,6]

**Results**

Figures 4 through 7 illustrate the type of data obtained. Blank runs were found necessary in some cases as a comparative standard because of the high rate of adsorption. Time lag and back mixing inherent in the system became appreciable despite

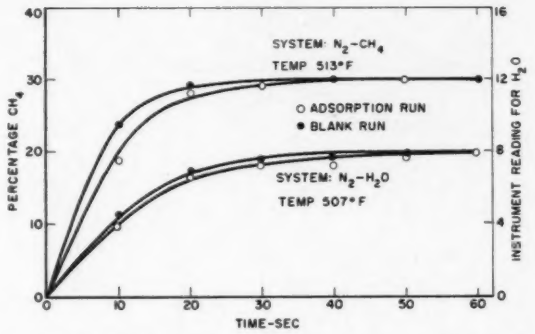


FIG. 6. COMPOSITION CURVES FOR $N_2$–$CH_4$ AND $N_2$–$H_2O$

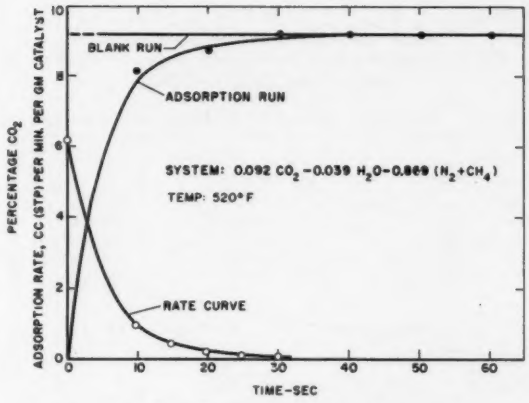


FIG. 7. COMPOSITION AND RATE CURVES FOR $N_2$–$CO_2$–$CH_4$–$H_2O$

precautions to minimize holdup. Figure 4 illustrates the type of data obtained using combustion analysis, and it also shows appreciable hydrogen adsorption on the catalyst. The rate curve is a derived curve based upon the composition and a material balance. The calculation method is illustrated elsewhere.[4] Figure 5, though also illustrating hydrogen adsorption, is of interest because the results are obtained indirectly, using the infrared analyzer. Figure 6 is illustrative of low adsorption results for methane and water, Fig. 7, of the moderate adsorption results for carbon dioxide.

## DISCUSSION

The $N_2$-$H_2$ and $H_2$-$CH_4$-$H_2O$ systems were studied at temperature levels of 500, 600, 700, and 750° F. Only hydrogen was appreciably adsorbed. Results correlated well, based upon the adsorption and dissociation of hydrogen on a dual catalyst site, as shown in Figs. 8 and 9. Such a mechanism is the expected one for hydrogen on nickel, according to previous results on metal-base catalysts.[1,7,8] As shown by Eq. 6, the slope and intercept of the lines yield the values of the constants $C_1 = \frac{sk_{H_2}C_t^{*2}}{2L}$ and $\frac{2sk_{H_2}}{LK_{H_2}}$, respectively. From these values $K_{H_2}C_t^{*2} = C_2$ is computed. Values of the constants are listed in Table I.

Plots of the constants $C_1$ and $C_2$ versus the reciprocal of the temperature are given in Figs. 10 and 11. These plots show that the sign of the slope of the straight lines is correct as predicted by the theory but that there is considerable variation of the values. The variation can be explained to some extent if one analyzes the probable error of the results, which was approximately 25 per cent of the value of the constants for the $N_2$-$H_2$ system and about 60 per cent of the value of the constants for the $H_2$-$CH_4$-$H_2O$ system. Better accuracy was obtained for the $N_2$-$H_2$ system because the method employed for measuring composition was more precise. Two points, $K_{H_2}C_t^{*2}$ for $N_2$-$H_2$ at 700° F, and $K_{H_2}C_t^{*2}$ for $H_2$-$CH_4$-$H_2O$ at 500° F, depart quite seriously from the linear relationship. This departure is inconsistent with the error spread and suggests experimental error.

The adsorption curves for methane and water, such as Fig. 6, show that these substances are only slightly adsorbed on the catalyst in the temperature range of interest in the reaction, 500 to 775° F. In a preliminary study of the system, Hottle[9] detected no adsorption for these gases. Binder and White[1] in their kinetic analysis assumed that the adsorption of these gases was negligible. On the basis of results of Hottle and of the present work, this seems quite justifiable. The discussion to follow therefore assumes negligible adsorption of methane and water. Minute amounts of poisons have been known to affect drastically the activity of catalysts. The results of this work showing slight adsorption of $CH_4$ and $H_2O$ are thus perhaps insufficient in themselves to indicate that their adsorbed forms have no influence on the surface catalyzed reaction. It is believed, however, that the results considerably strengthen similar conclusions based upon reaction kinetics alone.

A considerable effect of the presence of methane and water upon the adsorption rate of hydrogen is shown in Figs. 10 and 11, and also by Table II. This table compares ratios of the two constants for the two systems. These results suggest that if conclusions based upon adsorption results are to be applied to guide kinetics interpretation, all possible combinations of reaction system gases should be studied.

The presence of the unknown factor $C^*_t{}^2$ as a multiplier of the adsorption equilibrium constant prevented direct comparison with Binder and White's kinetically derived constants. Comparison of the energy of activation could be made, however, from

**TABLE I**

**RATE AND EQUILIBRIUM CONSTANTS**

| Temp. °F | $k_{CO_2} C_{l^*_2}$ | $K_{CO_2} C_{l^*_2}$ |
|---|---|---|
| **MECHANISM: $CO_2 + l_2 = 2CO_2 l$** | | |
| SYSTEM: NITROGEN-CARBON DIOXIDE-METHANE-WATER | | |
| 520 | 910±60% | 60±60% |
| 613 | 250±60% | 70±60% |
| 694 | 300±60% | 25±60% |
| 765 | 390±60% | 100±60% |
| **MECHANISM: $CO_2 + l_2 = CO_2 l + O{\cdot}l$; $H_2 + l_2 = 2H{\cdot}l$** | | |
| SYSTEM: NITROGEN-CARBON DIOXIDE | | |
| | $\frac{sk_{A_2} C_l^{*2}}{2L} = C_1$ | $K_{A_2} C_l^{*2} = C_2$ |
| 512 | 110±60% | 63±80% |
| 609 | 1050±60% | 60±80% |
| 713 | 40±60% | 18±80% |
| 765 | 130±60% | 130±80% |
| SYSTEM: NITROGEN-CARBON DIOXIDE-METHANE-WATER | | |
| 520 | 22±60% | 9±80% |
| 613 | 44±60% | 17±80% |
| 694 | 26±60% | 40±80% |
| 765 | 17±60% | 27±80% |
| SYSTEM: NITROGEN-HYDROGEN | | |
| 505 | 12±25% | 315±25% |
| 604 | 10±25% | 87±25% |
| 700 | 10±25% | 143±25% |
| 754 | 7±25% | 26±25% |
| SYSTEM: NITROGEN-HYDROGEN-METHANE-WATER | | |
| 504 | 29±60% | 450±60% |
| 599 | 150±60% | 3600±60% |
| 705 | 110±60% | 1120±60% |
| 753 | 130±60% | 1050±60% |

the effect of temperature on the combined constant. Such a comparison in Table III indicates considerable discrepancy between adsorption and kinetic results. The results of this work suggest a slight preference for mechanism "B" of the two alternate kinetic mechanisms proposed by Binder and White.

The carbon dioxide systems were also studied at four temperature levels in the range 500 to 765° F. Previous work on the adsorption of carbon dioxide indicates that it may be adsorbed as a molecule, dissociated into two portions, or even dissociated into three independent particles.[1,7,10]

Although Binder and White were able to obtain correlation of their kinetics assuming no dissociation of $CO_2$, the adsorption results of the present

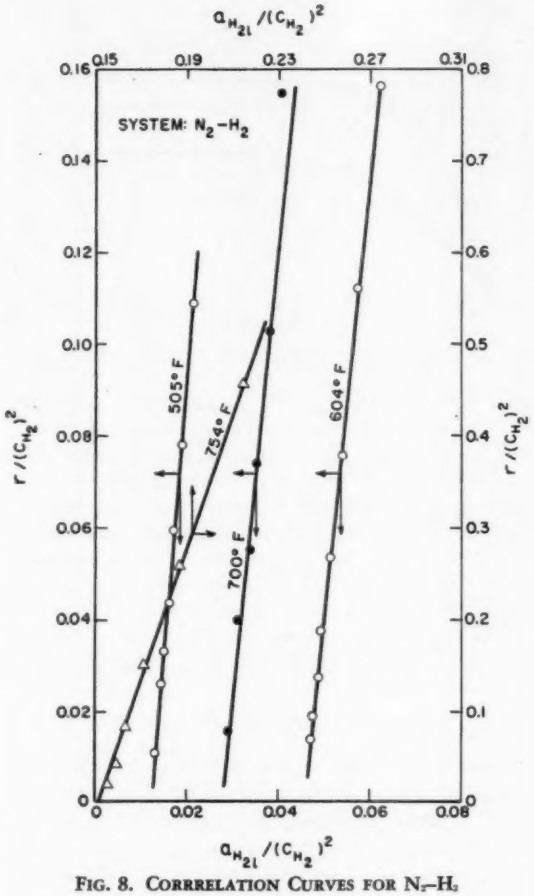


FIG. 8. CORRRELATION CURVES FOR $N_2$–$H_2$

**TABLE II**

**A COMPARISON OF THE CONSTANTS FOR THE SYSTEMS $N_2-H_2$ AND $N_2-H_2-CH_4-H_2O$**

| Temp. (°K) | $C_1$ for $N_2$–$H_2$–$CH_4$–$H_2O$ / $C_1$ for $N_2$–$H_2$ | $C_2$ for $N_2$–$H_2$–$CH_4$–$H_2O$ / $C_2$ for $N_2$–$H_2$ |
|---|---|---|
| 505 | 2.4 | .... |
| 602 | 15.0 | 41.4 |
| 702 | 11.0 | .... |
| 754 | 18.5 | 40.4 |

**TABLE III**

**SUMMARY OF STANDARD ENTHALPY OF ADSORPTION**

| Mechanism | Standard Enthalpy Change of Adsorption (Btu/lb mole) | |
|---|---|---|
| | $-\Delta H°_{H_2}$ | $-\Delta H°_{CO_2}$ |
| A | 34,500 | 19,700 |
| B | 24,250 | 16,260 |
| Present Research: 5,000–22,400 | | 5,180 |

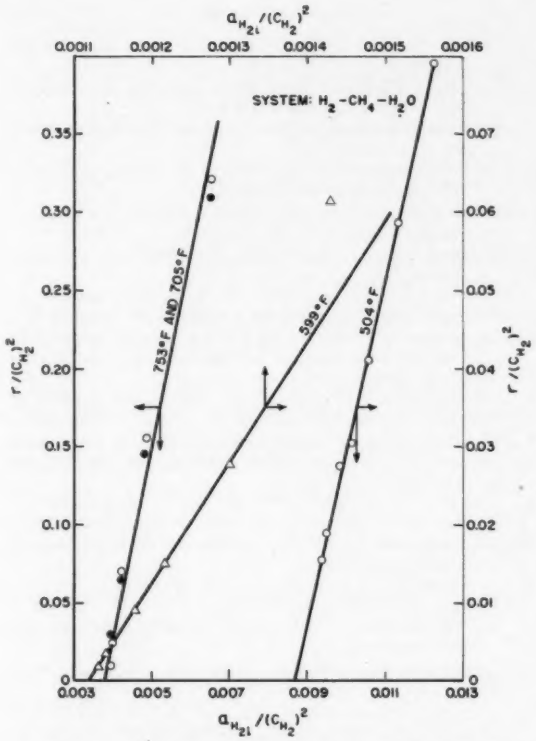


FIG. 9. CORRELATION CURVES FOR $H_2$–$CH_4$–$H_2O$

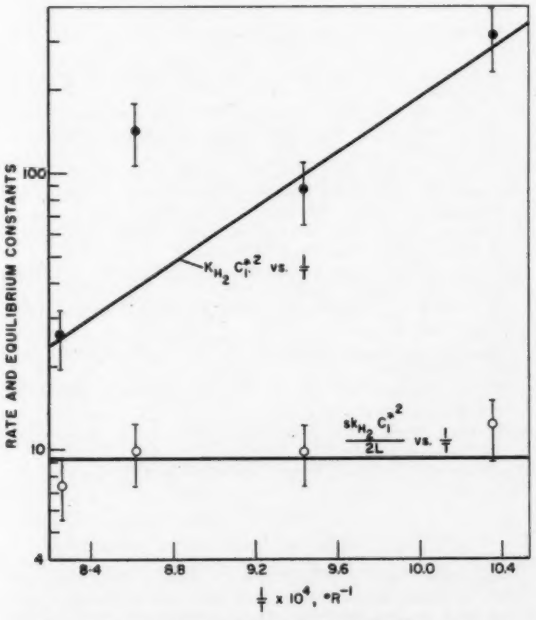


FIG. 10. RATE AND EQUILIBRIUM CONSTANTS *VS.* TEMPERATURE FOR $N_2$–$H_2$

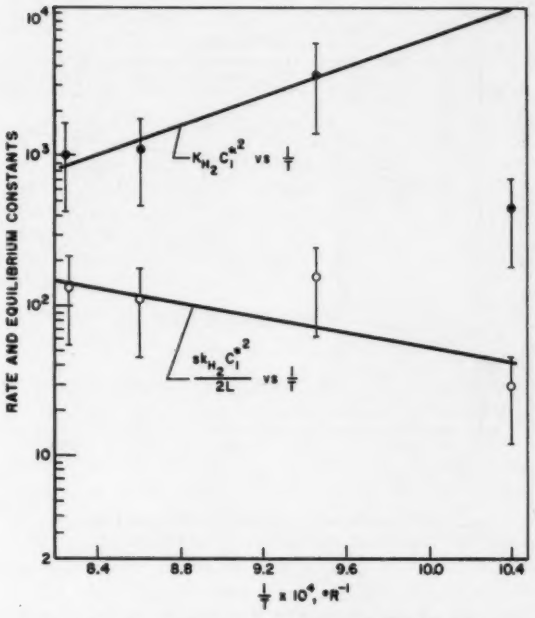


FIG. 11. RATE AND EQUILIBRIUM CONSTANTS *VS.* TEMPERATURE FOR $H_2$–$CH_4$–$H_2O$

work could not be correlated on this basis. Straight line plots were obtained, however, based either on dissociation on a dual site or bimolecular adsorption on a dual site without dissociation. Attempts to correlate the kinetic data of Binder and White based upon dual site dissociation failed. Therefore, the less usual mechanism of bimolecular adsorption on a dual site without dissociation was used in a successful correlation of their results. A comparison of the adsorption results (Fig. 12) and the kinetic results is given in Table III. This comparison also suggests a slight preference of mechanism "B" of the two proposed by Binder and White.

It should be recognized that the possibility of adsorption of carbon dioxide on dual sites, either dissociated or not, allows postulation of a rather large number of kinetic rate mechanisms. Only a few of these possibilities were explored in this work. It may be that a better agreement between kinetic and adsorption results could be attained with a mechanism as yet not thoroughly explored.

## CONCLUSIONS

The results of this research indicate that, for a fast adsorption reaction, only a moderate degree of accuracy can be expected with a flow system of the type used. Two problems are very serious in this type of measurement. The first is the time lag in the equipment of the measuring system itself. This problem affects the accuracy of the whole experiment.

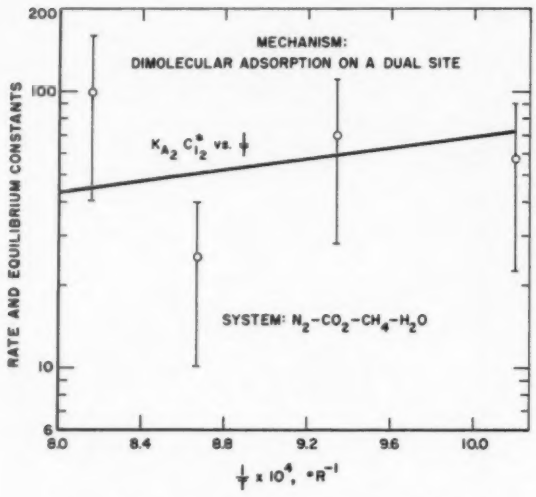


FIG. 12. RATE AND EQUILIBRIUM CONSTANTS *VS.* TEMPERATURE FOR $N_2$–$CO_2$–$CH_4$–$H_2O$

The second problem is the accuracy of the instrument. Unfortunately, for a fast reaction such as that studied in this work, further improvement is expected to be very difficult. For moderately slow reactions, this problem can practically be eliminated. Our work indicates that if the samples are collected and then analyzed individually, as was done for the $N_2$-$H_2$ system, better results are obtained. However, for a large number of runs this becomes tedious. The accuracy can also be improved by making several runs on each system at each temperature. This, again, could become quite tedious since close control of the temperature over long periods of time may be difficult. It is also probable that the infrared results could be improved considerably by means of a fast-response recording technique to replace sight reading of a microammeter.

The results of this paper have a large error which can be traced to a cumulative effect of the precision of the measurements. It was found that both hydrogen and carbon dioxide data can be correlated on the basis of dissociation on a dual site. The carbon dioxide data can also be correlated on the basis of adsorption of two molecules of carbon dioxide on a dual site. Further study showed that many other mechanisms were possible for this reaction, and that it is probable that the correct one has not yet been considered. Enthalpy calculations from this measurement and comparison with Binder and White's results[1] favored their mechanism "B." This mechanism involves the reaction of four dissociated hydrogen molecules with an adsorbed carbon dioxide molecule.

## NOMENCLATURE

$a_{Ai}$ = activity of $A$ at the interface for single site adsorption, in pressure units.

$a_{A2i}$ = activity of $A_2$ at the interface for dual site dissociation adsorption, in pressure units.

$C_A$ = concentration of adsorbed $A$, cubic centimeters (STP) per gram of catalyst.

$C_{A2}$ = concentration of adsorbed $A_2$, cubic centimeters (STP) per gram of catalyst.

$C_l$ = concentration of vacant active centers per gram of catalyst.

$C_{Al}$ = concentration of adsorbed dissociated $A_2$, per gram of catalyst.

$k_A$ = adsorption rate constant for the forward reaction in single site adsorption, per minute per atmosphere.

$k_{A2}$ = adsorption rate constant for the forward reaction in dual site dissociation adsorption, per minute per atmosphere.

$k'_A$ = adsorption rate constant for the reverse reaction in single site adsorption, per minute per atmosphere.

$k'_{A2}$ = adsorption rate constant for the reverse reaction in dual site dissociation adsorption, per minute per atmosphere.

$K$ = adsorption equilibrium constant in single site adsorption.

$K_{A2}$ = adsorption constant at equilibrium in dual site dissociation adsorption.

$K'_A$ = equilibrium constant for the dissociation step in dual site dissociation adsorption.

$L$ = concentration of active centers present initially per gram of catalyst.

$r$ = net rate of reaction in cubic centimeters (STP) of gas adsorbed per minute per gram of catalyst.

$s$ = number of equidistant active centers adjacent to each adsorption center in dual site dissociation adsorption.

Superscript (*) refers to equilibrium conditions.

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# Engineering Research Dividends

**Recent theses submitted for advanced degrees from the College of Engineering, University of Washington, will regularly appear in abstract form in *The Trend*. Complete copies of these theses are available for reference at the University of Washington Library. Address inquiries to the Director of the Engineering Experiment Station, University of Washington, Seattle 5.**

SEELEY, E. B., "The Snap-Action Bimetallic Thermal Disk and Its Application to Thermal Switches." M. S. in Mechanical Engineering, 1957.

Possible processes for forming bimetallic thermal disks were investigated. Prerequisites for a suitable process include low tooling cost, flexibility, and ease of control. The process requires that large groups of flat circular bimetal blanks be upset in such a manner that the two actuation temperatures of each disk be the same as the actuation temperatures of the rest of the group. The process should allow the two disk actuation temperatures to be arbitrarily chosen and obtained.

The process found to be most suitable uses a small drop-hammer with a convex, slightly pointed die and a flat rubber-padded die. By varying the height from which the hammer is dropped and by striking each disk twice (once on each side) the actuation temperature can be arbitrarily chosen and obtained, and the process is repeatable within small temperature tolerances. For a given disk diameter almost any two arbitrarily chosen actuation temperatures up to 500° F can be obtained with one set of dies.

Stability of the disk actuation temperatures was found to be dependent on proper heat treatment of the formed disks.

SIDDIQUI, S. H., "Minor Losses in Viscous Flow." M.S. in Civil Engineering, 1958.

Although the subject of friction loss for laminar or viscous flow of fluids in pipes has received considerable attention, little seems to be known about other losses. The object of this study was to investigate the nature of abrupt expansion loss, and bend or elbow losses, where the flow in the piping is laminar, or at least with Reynolds number well under the critical value of 2,000.

The results of a rational theory presented for abrupt expansion under viscous flow conditions, in which eddies are not included, are compared with those of an experimental laboratory investigation made by the writer. These results are in acceptable agreement with each other. No theoretical expression for elbow loss was found in a search of the literature, and none was devised in this paper. However, experimental data were obtained, and a comparison is made with published values for elbow losses for conventional turbulent pipe flow.

These losses (abrupt expansion and elbow loss) may be major items in simple and short passages; on the other hand, they may be considered minor losses in long ducts or pipe lines where pipe friction predominates.

TASHIRO, S., "A Study of Flux Distribution and Reactivity for a Spherical Intermediate Reactor Employing an Iterative Technique for Solving the Diffusion Equations." M.S. in Electrical Engineering, 1958.

Intermediate reactors are rapidly taking their place alongside thermal reactors in relative importance. However, because of the wider energy range of fission neutrons in an intermediate system, analysis becomes difficult and multigroup calculations must be performed, even for qualitative results.

In 1955 Mandl and Howlett, of the United Kingdom Research Establishment, published a method of calculating the critical mass of an intermediate reactor which introduced a numerical means of solving multigroup equations.

In the present thesis this numerical method has been developed, programmed on the IBM 650 digital computer of the University of Washington, and results obtained using data compiled from an intermediate assembly by Ehrlich and Hurwitz of Knolls Atomic Power Laboratory.

The multiplication rate and flux distribution in the core are plotted for a spherical intermediate reactor with varying core and reflector thicknesses, and comparisons are made between intermediate and thermal assemblies for these two reactor variables.

The application of this numerical method to reactors of other geometrical shapes, such cylindrical and parallelepipedal, are also briefly discussed.

*LEFT*

Members of panel discussion on personnel problems.

*Left to right:* Professor A. L. Miller, U. of W.; R. P. Rodgers,, Olympia; O. R. Dinsmore, Olympia; C. C. Arnold, Seattle; J. W. Arrasmith, Spokane

*RIGHT*

Group of members of the Oregon State Highway Department. *L. to r.:* G. Le Tournoux, L. H. Young, Tom Edwards, D. J. Barbee.

*BELOW*

*Left*

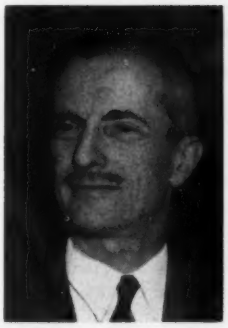
Some members of the panel on highway planning. *L. to r.:* C. K. Glaze, Olympia; James York, Seattle; Wm. Hall, Portland; Prof. E. M. Horwood, U. of W. Not shown, Prof. M. R. Wolfe, U. of W., chairman.

*Right*

*L. to r.:* E. A. Cowell, Chairman of the Washington State Highway Commission, who gave the opening address of the Conference; H. O. Walberg, Lane Co. Engineer, Oregon; Prof. Martin Coopey, O.S.C.

# Road Builders Hold Eleventh Annual Meeting

R. G. HENNES
*Professor of Civil Engineering*



R. G. Hennes

The Northwest Conference on Road Building, which holds alternate meetings at Oregon State College (Corvallis) and at the University of Washington, met February 20-21 at More Hall, under the sponsorship of the Department of Civil Engineering. The meeting was attended by a representative group of engineers from federal, state, county and city agencies and from private practice, although the pressure of the present high tempo of road-building activity tended to depress the total registration below the record of previous years.

The keynote address was given by E. A. Cowell, Chairman of the Washington State Highway Commission. The other commissioners also came from Olympia for the Conference. Mr. Cowell reviewed the present status and future prospects of the highway program. The intensification of the road-building effort as a result of the new federal highway policy has been successfully accomplished in the state of Washington. As the program gets into full swing, the future need for more men and money becomes apparent.

Professor Martin Coopey of Oregon State College headed a panel on public relations. Don Brown, Public Information Officer of the Washington Highway Department, started the discussion, pointing out that the public contacts of departmental employees are more significant in this area than official press releases. Russell Van Rooy of the Washington Automobile Club stressed the importance of public appearances by the rank and file of professional workers in a highway department, rather than limiting such contacts to the executives. An especially welcome member discussant was H. O. Walberg, formerly Skagit County Engineer and now County Engineer of Lane County, Oregon, who spoke of public relations at the county level.

The second panel was devoted to personnel problems, with Professor A. L. Miller (Civil Engineering) serving as moderator. O. R. Dinsmore, Assistant Director of the Washington Highway Department, described a successful trial program in which forty high school graduates were given a two-month training course in highway engineering techniques. C. C. Arnold, Seattle consulting engineer, described how a public official can most effectively select private consultants to relieve his shortage of professional manpower. John W. Arrasmith, Spokane County Road Engineer, told of the program undertaken by the Washington State Associations of County Commissioners and County Engineers to attract competent engineers into county work. This includes a study of functions, exchange of information on vacancies and applicants, and the summer employment of engineering students. R. P. Rodgers, B.P.R. Divisional Engineer for Washington, pointed out the need to utilize the available supply of engineers more effectively. This means supplying both human and mechanical assistance to take over routine functions such as tabulating, plotting, and calculating.

Professor M. R. Wolfe of the Department of Architecture and Urban Planning, moderated a panel dealing with the bases for highway planning. Professor E. M. Horwood (Civil Engineering) discussed the confluence of highway planning with urban planning in our metropolitan areas, emphasizing the problems arising in the design of urban freeway systems. C. K. Glaze, head of the Washington Highway Department's Planning Survey, explained the techniques employed in modern highway planning, such as traffic counts, origin-destination surveys, cost-benefit analyses, and sufficiency ratings. James York, of Larry Smith & Company, Seattle, described the changes in land use that developed especially at freeway interchanges, with far-reaching effects on the economic structure of pre-existing communities.

A panel on the use of electronic computers, headed by Professor L. J. Lewis (Electrical Engineering), included an introduction to modern civil engineering usage of the computer by Professor J. E. Colcord, and descriptions of current highway department computer practices by George Le Tournoux of Salem and R. J. Hansen of Olympia. Mr. John L. O'Day, of I.B.M., explained the capability and availability of the electronic computer. Some of the different jobs being done as routine assignments include:

1. Grade profile and road design
2. Earthwork calculations
3. Traverse closure problems
4. Bridge design
5. Right-of-way computations
6. Origin and destination studies

7. Freeway assignment problems
8. Monthly equipment summaries
9. Statistical studies
10. Soil analysis
11. Bid-letting computations

The fifth panel was planned to encourage discussion of various unrelated timely topics. Under the chairmanship of Professor Martin Ekse (Civil Engineering), problems of accounting, traffic, and administration were considered. K. F. Jones, Pierce County Engineer, urged that the records of the county road department should be kept in no greater detail than their subsequent use would justify. The county engineer should first decide why he wants records, and then determine what sort of records would meet his needs. Professor Sawhill (Civil Engineering) called attention to developing problems of highway traffic that warrant research and perhaps modification of present design practices. The increased acceleration of the new automobiles has made obsolete the present accepted values for safe passing distance. The lower new cars provide less sight distance, which should be reflected in modified road curvature standards. Skid resistance and road roughness should be studied to obtain more reliable quantitative values. Neglect of residential street traffic problems is a source of relatively many accidents. W. H. Landaas and D. J. Evans, of the Asosciated General Contractors of America, discussed contractual aspects of the road-building problem. Economies could be realized through uniformity and simplicity in contract specifications. It is highly desirable that there be a common understanding about the meaning of the specifications, not only among the parties to the contract but also among all the owners' representatives who make contact with the contractor.

Professor E. A. Sibley, of Oregon State College, was moderator of a panel on subsoil exploration. L. H. Young and D. J. Barbee of the Oregon Highway Department described practices in their state. Mr. Young gave four objectives of subsoil exploration: (1) to recognize excavated soil which is suitable for placement in the top 2 or 3 feet of the subgrade; (2) to determine the stability of embankment foundations; (3) to obtain information about ground water; (4) to locate suitable borrow material. Considerable reliance is placed upon geological information. Mr. Barbee talked on the use of seismic refraction. The geophysical crew in Oregon covers about 50 projects a year, with an estimated accuracy of 5 per cent in seismic work and 10 per cent in electrical resistivity work. He pointed out that (1) seismic procedures must be calibrated through test pits and dull holes, (2) seismic prospecting cannot reach a low-velocity material underlying a high-velocity material, (3) trained personnel are essential to the proper interpretation of seismic data.

J. H. McLerran, assistant chief of the Photographic Interpretation Research Branch of the U. S. Army Snow Ice and Permafrost Research Establishment, was the first speaker on the Subsoil Exploration panel. He pointed out the value of air photos for the following uses:

1. Preliminary interpretation of soils and other natural environmental factors during the planning, reconnaissance survey, and preliminary survey stages
2. Engineering soils maps along proposed locations
3. Location of construction materials

Airphoto interpretation is based upon the similarity to be found in airphoto patterns where similar soils have similar topographic and climatic conditions. The elements that singly or together form a significant pattern are landform, drainage system, erosion characteristics, photo tones, vegetation, and land use.

Stanley D. Wilson (of Shannon and Wilson, Seattle) spoke on the detection of landslides. Major slope failures are preceded by measurable strains. For the measurement of horizontal ground movements to a depth of several hundred feet the "Slope Indicator" has been developed. This consists of a pendulum pivoted on ball bearings and enclosed in a watertight brass cylinder of about 2.5 inches outside diameter and 15 inches long. The tip of the pendulum is in contact with a precision wound resistance coil. This underground assembly forms half of a conventional Wheatstone bridge circuit, the other half being in a control box above ground. The inclination of the tiltmeter is proportioned to the dial reading of a precision potentiometer in this control box. The instrument measures deformations as small as one inch in one hundred feet of depth. So far it has been used to measure lateral spreading of clay layers under ore yards, deformations behind walls and bulkheads, movements associated with subsidence, and dam foundations.

Tom Edwards, construction engineer with the Oregon Highway Department, described slide stabilization methods employed in Oregon. Investigation of a suspected area involves several steps:

1. Depth investigation by vertical auger holes or shafts
2. Check of fringe area for water sources such as ponds or streams
3. Possible use of dye to check migration of ground water from an upper area to the suspected zone
4. Geophysical exploration
5. Water table determination
6. Location of slip planes

Chief reliance is placed on drainage as a means of ground-water control.

If preventive methods fail and a landslide does occur, prevailing practice favors the use of horizontal drilled drains in pervious soils, and partial excavation plus surface-water collection in the case of impervious soils.

# OUTSIDE U. S. A.

## Highlights from Our Foreign Exchange Publications

RUPTURE BY BENDING AND BY SHEARING STRESS IN REINFORCED CONCRETE BEAMS. R. Chambaud, *Annales de l'Institut Technique du Batiment et des Travaux Publics,* Feb., 1957. French.

The author first summarizes and completes the theory expounded in his previous papers on rupture under bending stress. He then covers the principal object of this work and deals with rupture under shearing stress, a subject still in scientific evolution. When rupture tests are carried out on test-pieces calculated by conventional rules for bending and shearing, the rupture almost always occurs in bending, almost never in shear. Also, when a test beam has a sufficiently high flexural resistance to permit rupture under shear, the effective resistance is generally very much higher than would be indicated by conventional calculation with a normal safety.

These experimental results are the basis for the present study on shear stress. The results suggest that the resistance would be assured by using concrete struts more inclined than indicated by the classical theory, the member in certain respects acting like a subtended arc and in other respects like a multiple lattice, with members in tension formed by the stirrups and with members in compression formed by the struts.

The theory resulting from these observations confirms the soundness of the original hypothesis. It shows the possibility of making large economies in stirrups in reinforced concrete beams, especially in current floor construction.

The third part of the paper deals with numerical applications to beams breaking under simple compound bending or by shear stress. The fourth part comments on photographs of beams ruptured under various conditions. In the case of rupture under shearing stress, the second network of cracks, steeply inclined, anticipated by the theory and confirmed by experience, was evidenced by the photographs.

CONTRIBUTION TO THE STUDY OF PROBLEMS IN THE UTILIZATION OF LIGHT-WEIGHT CONCRETES, H. Bodecher. *Annales de l'Institut Tech. Bat. Trav. Pub.,* Dec., 1957, French.

Procedure of making "Siporex" cellular concrete is described. The constituents are Fontainebleau sand, binder, and aluminum powder, treated in the autoclave in such a way as to produce a silicocalcareous reaction. Its density may vary from 0.4 to 0.8, and its strength is such that it may be used for bearing walls on several storeys. The author describes various examples of the use of "Siporex," in particular the construction site at Noisy-le-Sec, of which details and cost are given.

NOMOGRAPHIC METHOD FOR EVALUATING X-RAY BACK-REFLECTION PATTERNS USED IN THE COMPUTATION OF RESIDUAL STRESSES IN STEELS. I. S. SZANTO. *Period. Polytech.* (Budapest), 1957. English.

Measurements of stresses, i.e., lattice strains, in metals by X-Ray diffraction patterns are usually performed by using the back-reflection arrangement. Two methods are most frequently used for evaluating these patterns, the so-called reflectograms: (1) by determining the shift of diffraction line peaks, caused by an appropriately indicating array of atomic planes, (2) by analyzing the profile of the interference lines.

Application of both methods appears to be most favorable, if permitted by test conditions, first of all by metallographic conditions of the specimen investigated. Criteria for the latter, as well as the computation of a new parameter of state rationally indicating the material's intrinsic properties, i.e., internal stresses, to be obtained from complex evaluation have been dealt with by the author elsewhere.

However, for production routine measurements of an informative character, a rapid and not too complicated method has to be developed, so as to provide for an easier evaluation of reflectograms, ensuring the relative minimum for possible errors. Plotting recorded data into nomograms appears to be a most desirable solution.

The scope of the present paper is to try to develop a method for the graphic evaluation of X-ray back-reflection patterns, ensuring an accuracy generally satisfactory for common requirements, but simple enough to dispense with the use of qualified labor for performing the actual measurements.

HEAT TRANSFER DURING NUCLEATE BOILING OF LIQUIDS UNDER CONDITIONS OF NATURAL CONVECTION, B. Staniszewski. *Bull. Acad. Pol. Sci.,* V-2, 103-5 (1957). English. 103-5 (1957). English.

**Reviewed by M. M. David, Associate Professor of Chemical Engineering**

By using the same qualitative picture of natural convection boiling as employed by Rohsenow,[3] the author has derived, through dimensional analysis, an equation of the Dittus-Boelter type for correlating nucleate pool-boiling heat transfer data. The final equation is somewhat similar to the Rohsenow equation in form, but does not appear to have the general applicability of either the Rohsenow or Forster-Zuber[1] equations. Experimental data for three systems (distilled water, trichlorethylene, and carbon tetrachloride, boiling on a platinum wire) have been used to determine the constant and exponents in the proposed equation.

The author also presents equations for predicting the first and second critical points in pool boiling (the latter being the heat flux at which film boiling reverts to nucleate boiling). Experimental data are used to evaluate constants and exponents specific for each substance. These equations do not seem to be as generally useful as other available correlations[2] for the first critical point, but are unusual in predicting the second.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2. McAdams, W. H., *"Heat Transmission,"* 3rd Ed., McGraw-Hill Book Co., Inc., New York (1954).
3. Rohsenow, W. M., *Trans. A.S.M.E.,* 74, 959 (1952).


STEEL AT HIGH ELASTIC LIMIT IN WELDED CONSTRUCTION. M. J. Guerin. *Annales de l' Institut Technique du Batiment et des Travaux Publics.* Feb., 1957. French.

In the welding of steel of high elastic limit certain difficulties occur when it is brittle and self-tempering. Following an incident, the French National Railways undertook welding tests on the base metal. The following points were examined:

1. Effects of the chemical composition of the steels.
2. Effects of the methods of working the metals.
3. Effects of the mechanical properties of the finished article.
4. Hardness under weld fillet.
5. The idea of the carbon equivalent.
6. The brittleness.
7. The rapid control of weldability by the Kommerell test.

The author then deals with the thermal conditions of welding and compares manual and automatic welding under flux.

As a result of these tests the specifications of the French National Railways have laid down the characteristics of weldable steel and the directions for welding operations.

# Notes and Comments

## ENGINEERS IN THE NEWS

Research carried on by the Departments of Chemistry and Chemical Engineering will be reported in three papers to be presented before the Cellulose Division of the American Chemical Society at its meeting April 13-18 at San Francisco. This research is supported in part by the Pulp Mills Research Program. Dr. **J. V. Moacanin,** former graduate student, now a Senior Research Engineer at the Jet Propulsion Laboratory at C.I.T. will present "Lignin: Estimation of Polymolecularity in Lignin Sulfonate Polymers from Diffusion Measurements." Co-authors are former graduate student, **H. Nelson,** now with the Hanford G. E. Engineer Works, Dr. **E. Black,** former Scandanavian-American Research Fellow, now with the Forest Products Research Laboratory at Stockholm, **V. F. Felicetta,** Research Assistant Professor, and **J. L. McCarthy,** Professor of Chemical Engineering.

The second paper, "Lignin: Isolation of Low Molecular Weight Sulfonates from Spent Sulfite Pulping Liquors," will be presented by **D. Glennie,** former graduate student and Hooker Electrical Company Research Fellow, now Head, Chemical Division, Oregon State Forest Products Laboratory. Co-authors are Professors **Felicetta** and **McCarthy.** Professor **Felicetta** will present the third paper, "Lignin: Identification and Synthesis of a Sulfonated Lignin-like Monomer Isolated from Spent Sulfite Liquor." Co-authors are **M. Andrus, S. Schubert, D. Glennie,** and **J. L. McCarthy.** Dr. Andrus, former graduate student and Rayonier Research Fellow, is now Research Chemist with the Rohm & Haas Company, Philadelphia. Mr. Schubert is a graduate student and present holder of the Hooker Company fellowship.

Dr. **McCarthy** will also participate in a symposium on "Wood as a Chemical Raw Material" and will preside at a session of a symposium on "The Chemical Nature of Wood and Bark Constituents."

Several members of the Department of Civil Engineering appeared on the discussion panels of the Northwest Conference of Road Builders, held on the campus, February 21, 22. **J. E. Colcord,** Associate Professor, spoke on "What the Average Engineer Should Know About Electronic Computers," **R. B. Sawhill,** Assistant Professor, dealt with "Correlation of Research and Highway Design Elements," and **E. M. Horwood,** Associate Professor, reported on "The Federal Interstate Highway Program and the City Center."

**D. L. Anderson,** Associate Professor of Mining Engineering, at the meeting of the Pacific Northwest Regional Conference of the A.I.M.E., to be held at Seattle, April 17, will present a paper on "Shaft Sinking and Development under Hot-Water Conditions."

**A. L. Miller,** Professor of Mechanics and Structures, who gave a paper on "Warping of Reinforced Concrete" before the Northwest Regional meeting of the American Concrete Institute last November, attended the A.C.I. convention held in Chicago during February, where he took part in further discussion of his paper before the Research Section. While in Chicago he also attended the annual meeting of the A.S.C.E. where, on February 27, he presented a paper by **D. D. Vasarhelyi,** Associate Professor of Civil Engineering, on "The Effects of Fabrication Techniques on Bolted Joints." Dr. Vasarhelyi is in charge of the Bolted Joints Project sponsored by the Research Council on Riveted and Bolted Structural Joints.

**B. W. Owens,** Associate Professor of Mechanical Engineering, attended the meeting of the American Institute of Industrial Engineers in Seattle, March 12. The subject of his paper was "Is Random Work Simplification Representative?"

## SEWAGE WORKS SCHOOL

The Sixth Biennial Sewage Works School was held at the University March 13-14. Classes were provided for beginning, intermediate, and advanced registrants. Total student attendance was 103. Professor R. B. Van Horn, Executive Officer of the Civil Engineering Department, gave the welcoming address.

Classes and laboratory demonstrations covered all the chief methods used in sewage treatment plants. University faculty and staff members who acted as instructors were R. O. Sylvester, Professor of Sanitary Engineering, H. K. Moritz, Professor of Hydraulics, R. H. Bogan, Assocaite Professor of Civil Engineering, T. C. Campbell, Professor of Civil Engineering, and W. Maske, Sanitary Chemist, Department of Civil Engineering. Other lecturers were drawn from the Washington State Pollution Commission, State Department of Health, and various municipal and industrial agencies.

## NEW CHROMITE EXTRACTION PROCESS

A research project carried on under the supervision of F. B. Brien, Associate Professor of Mineral Engineering, with the cooperation of the Northwest Experiment Station (U. S. Bureau of Mines), may open up commercial mining possibilities in the Twin Sisters area. The new flotation process would permit recovery of 93 per cent of the chromite in the ore deposits of that region, in comparison with 80 per cent obtained by present extraction methods. Moreover, the chromite would be of better quality.

Working on the project under Professor Brien is Evan Lowe, graduate student in Mineral Engineering, who has completed his thesis and will receive his M.S. degree at the end of the spring quarter.

## STUDY OF A SOLID-STATE REACTION

*(Continued from page 9)*

of reaction behavior and require an activation energy similar to that necessary for the diffusion of chromium in steel.

Hardness and electrical resistance data indicate that the initial chromium carbide particles first form coherently with the matrix, then break away to establish finite interfaces. They also show that matrix changes are encountered that are not reflected in the composition of the carbides.

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### ACKNOWLEDGMENTS

**The author would like to acknowledge the assistance provided by Mr. James V. Alger of the Bettis Atomic Power Division, Westinghouse Electric Corporation, Pittsburg, Pennsylvania, former graduate student in the Division of Metallurgical Engineering at the University of Washington. Mr. Alger obtained many of the data used in establishing the calibration curve used in this work.**


## PROFESSIONAL ETHICS

### *A Rejoinder*

*(Continued from page 2)*

**Historically speaking, philosophy is becoming the philosophy of science. As traditionally formulated, ethics has little to offer engineers in the way of substance—or logic. The *logic* of technical judgments and the *logic* of ethical judgments is identical. The distinguishing feature is found in the character of data *within the logical scope* of ethical judgments. Technical judgments do not involve consideration of ends or ultimate values. In ethical judgments, ends or ultimate values have the *logical status* of factual data. In the social sciences, the facts of social, economic, and political life also have a dual logical status. They have the logical status of brute facts, and they also have the logical status of social values. Intimate knowledge of the changing fact-values of modern society provides the only naturalistic basis for developing a superior sense of values. A balanced education for modern living involves more than a knowledge of techniques—it involves an understanding of, and commitment to, the fundamental rationality of practicing a high degree of tolerance, objectivity, and integrity in conjunction with a highly developed sense of social responsibility.**

**Current pressures will very likely modify engineering curricula in two ways. Pre-engineering education is due to receive the emphasis found in pre-law and pre-medical education. In addition, engineering curricula will be eventually extended to the fifth and sixth years. Much of the emphasis in these terminal years will be of an advanced technical nature. The remainder, however, will very likely be oriented to the social sciences and the humanities. In this area, the core of emphasis will be upon sociology, economics, and psychology. The better engineering schools will very likely bracket this core with elective courses in cultural anthropology, business, literature, and philosophy.**

**The responsibility for making the key decisions involved in the revision of engineering curricula now rests with educators and engineering faculties. In the long run, however, the broad changes in our social norms will determine both the future requirements for engineering education and the professional status of engineers.**

## NEW TECHNIQUES IN PHOTOELASTICITY

*(Continued from page 16)*

the same end results as either of these two techniques. The advantage of using fringe sharpening and fringe multiplication rather than a compensator lies primarily in the fact that a complete picture of the fringe order distribution can be obtained in one operation.

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## Aspects of Modern Engineering Education

*(Continued from page 1)*

proud of their total ignorance of science. And I do think that as the engineering educators do devote so much serious thought to their curricula, graduates of science and engineering courses may, in fact, become presently the liberally-educated citizens of this breathless age.

But to impart a broad appreciation of the humanities and of social studies—to expect to inculcate some appreciation of history, art, music, literature, economics, philosophy, and sociology within the framework of a respectable engineering course—is, of course, impossible, for it succumbs again to the deadly effect of sacrificing scholarship in depth, to studies in breadth—the horrible survey courses. Our attempt to cope with such a difficult situation has resulted in a broad band of elective courses in the humanities from which a choice must be made in second and fourth years, and only in a large dose. Of course this will allow an engineer to graduate with large areas of total ignorance, but at least in the subject of his choice sufficient depth may have been probed to stimulate curiosity and engender an appreciation of scholarship which will never leave him. One of our great chemical engineers, the late A. P. Colburn, described a salesman explaining his failure on a particular account by taking refuge in the time-weary excuse, "You may lead a horse to water but you can't make him drink." His exasperated manager exploded, "Your job isn't to lead him to water, or to make him drink either! It's to make him realize how thirsty he is!" This, then is our philosophy with regard to the humanities—to present sufficient opportunity for the student to become curious about a subject of his choice, and to leave the rest up to the enquiring minds we are trying to cultivate. Accordingly, we are allowing about 18% of our engineering curriculum to humanities and social studies....

This month the philosophy seems to be to look at the sky and exhort our scientists and engineers to "get in there and research the hell out of it!" While this awakened interest in research is gratifying, it is nonetheless depressing that it has its roots in apprehension. It is terror, and not intellectual awakening which is causing the stirrings beneath the surface of our complacency about the woeful disregard for the value of time which has pervaded our primary and secondary education on this continent. And because fright is a fleeting emotion we must be careful that our reassessment of educational values is based on sober, long-range, mature judgments.

## Vehicle Maintenance and Fleet Supervisors Courses Held on Campus

The Seventh Annual Motor Vehicle Maintenance Conference was held at More Hall, March 24-26. It was sponsored by the Departments of Civil and Mechanical Engineering and the School of Forestry, in addition to the Auto Club of Washington; Northwest Section of the S.A.W.; Seattle Chapter, National Association of Fleet Supervisors; King County Safety Council; Washington Motor Coach Association; and Washington Motor Transport Association. Some 60 manufacturers' representatives, chiefly from California, Oregon, and Washington were enrolled. Fred H. Rhodes, Jr., Professor of Civil Engineering, was director of the Conference.

According to the usual procedure, panels were devoted to specific types of maintenance problems and registrants were grouped according to the vehicle classification and/or use in which they were interested.

Group 1 included light and medium duty deliveries; Group 2, transfer, such as fuel and premix; Group 3, highway departments, contractors, and heavy construction; Group 4, buses; Group 5, over-the-road operations; Group 6, logging; Group 7, utilities. Group 7 was included this year for the first time.

In 1952, 46 were enrolled for the First Conference; in 1957, 308 were enrolled. This year 375 certificates were awarded at the close of the course.

The Fifteenth Annual Training Course for Motor Vehicle Supervisors will again be so fortunate as to have Professor Amos E. Neyhart as program coordinator. Professor Neyhart is Administrative Head, Institute of Public Safety, Pennsylvania State University, Consultant on Road Training for the A.A.A., and has acted for many years as consultant for large fleets throughout the United States.

The training course, to be conducted by the University College of Engineering and cooperating agencies, will be held on the campus April 14-18, opening with a welcoming address by Dean Harold E. Wessman. The program covers five main divisions:

I Good drivers—how to pick them
II Training in small fleets and large
III Supervision—organizing for smooth operation
IV Records—a guide to lower costs
V Creating and maintaining interest

Sponsoring agencies, in addition to the College of Engineering, include the Automobile Club of Washington, Seattle Chapter, National Association of Fleet Supervisors, Seattle Engineering Department, King County Safety Council, Seattle Police Department, Washington Drivers Safety Center, Washington Motor Coach Association, Washington Motor Transport Association, Washington State Office of Public Instruction, and Washington State Patrol.

Professor Rhodes is also director of this course.

# PUBLICATIONS

*of the*

# ENGINEERING EXPERIMENT STATION

## UNIVERSITY OF WASHINGTON

Requests for copies of publications should be addressed to the Director, Engineering Experiment Station, University of Washington, Seattle 5.

## BULLETINS

48. The Influence of Pipe Thickness on Re-Entrant Intake Losses. Charles William Harris, 33 pp. 1928.
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55. Vacuum-Tube Control for Electric Wind-Tunnel Balances. Fred S. Eastman. 20 pp. 1931.
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58. Preliminary Tests of Thirteen Washington Coals in a Powdered Coal Boiler Plant at the University of Washington. George Samuel Wilson, Harry Fagan Yancey, and Joseph Daniels. 27 pp. 1931.
60. An Electromagnetic Balance for Force Measurement of Current Control. Fred Scoville Eastman. 29 pp. 1932.
61. Hydraulic Flow Characteristics of a Square-Edged Intake. Charles William Harris. 21 pp. 1932.
67. The Doherty Washer Cooler. Sybren Ruurd Tymstra. 61 pp. 1932.
69. Studies in Hydrogenation of Certain American Coals. Warren L. Beuschlein, Bert E. Christensen, and Calvert C. Wright. 24 pp. 1933.
72. The Derivation of the Mean Temperature Difference Between a Saturated Gas and a Cooling Liquid, and also the Derivation of the Mean Velocity of Such Gas. Sybren Ruurd Tymstra. 19 pp. 1933.
74. The Deformation of Hard Grade Reinforcing Steel During and After Construction in a Reinforced Concrete Building. Sergius Ivan Sergev. 33 pp. 1933.
75. The Water Tube Gas Condenser. Sybren Ruurd Tymstra. 24 pp. 1934.
77. A Study of Fundamental Relations of the Mathematical Theory of Elasticity. Arthur Melvin Winslow. 25 pp. 1934.
81. Influence of Two Secondary Factors in Weir Measurement. Charles William Harris. 16 pp. 1935.
84. Equations for Calculating Three Phase Symmetrical Components. Gordon Russell Shuck. 32 pp. 1935.
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